

AMBIENT HYDROCARBONS IN THE HOUSTON METROPOLITAN AREA DURING
TEXAQS 2000: AN IDENTIFICATION OF UNUSUAL FEATURES

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Abstract

Houston's ozone problem has been linked to the occurrence of very high light olefin concentrations. We have analyzed the DOE G-1 aircraft hydrocarbon data set to provide additional information on the geographic distribution and prevalence of air samples with high olefin concentration as well as an identification of other compounds which contribute to the high hydrocarbon reactivity in Houston. In order to identify high concentrations we need a definition of normal. For that purpose we use aircraft samples collected during a 1999 aircraft based field campaign in Philadelphia relying on the circumstance that the frequency distributions of NO_x and C_2H_2 in Philadelphia are nearly the same as in Houston. Comparison is made also with hydrocarbons collected in Phoenix which exhibit nearly the same NO_x and C_2H_2 frequency distribution as the other 2 cities, but in spite of that similarity have a much lower hydrocarbon reactivity. As in other studies we find that there is a subset of Houston hydrocarbon samples with very high OH-reactivity due to elevated concentrations of ethylene, propylene and less often butenes, including 1,3 butadiene. Although these samples stand out as being qualitatively different we present evidence that ethylene and propylene are significantly elevated in at least half of the Houston samples, covering a wide geographic area apart from the Ship Channel region. Frequency distributions for these compounds are log normal suggesting that Houston's atmosphere is a single entity rather than separate industrial and urban areas. The comparison between Houston and Philadelphia also identifies $\text{C}_2\text{-C}_5$ alkanes, n-hexane, and benzene as having elevated concentrations. Emission reductions of these less reactive compounds sufficient to yield the concentrations observed in Philadelphia would have a minor effect on the most reactive samples, but about a 20% effect on samples with more typical (median) reactivity.

Introduction

Results from the TexAQS 2000 field campaign indicate that the concentration of light olefins (ethylene, propylene, and butylenes) in the Houston metropolitan area are significantly greater than can be expected from emission inventory estimates [*Ryerson et al.*, 2003; *Wert et al.*, 2003]. Petrochemical plants responsible for the very high light olefin emissions contain large NO_x point sources due to the requirements of these facilities for electric power, process heat, and the flaring of excess hydrocarbons [*EPA*, 2004]. Light olefins react rapidly with OH radicals and in the presence of sunlight and high NO_x concentrations, O₃ is produced rapidly [*Kleinman et al.*, 2002; 2004a]. Photochemical transport models in which light olefins emission rates have been increased several-fold to match observations indicate that Houston's very high peak O₃ concentrations are caused by light olefin emissions in excess of inventory estimates [*Jiang and Fast*, 2004; *Lei et al.*, 2004; *Zhang et al.*, 2004]. This conclusion is supported by case study analysis of O₃ episodes [*Berkowitz et al.*, 2004; *Daum et al.*, 2004a, b].

In this report we present a further analysis of hydrocarbon measurements, primarily based on samples collected by the DOE G-1 aircraft. This report has 2 foci:

- To show the pervasiveness of elevated light olefin concentrations in samples taken throughout the Houston metropolitan area.
- To determine whether Houston has elevated concentrations of other hydrocarbons, besides light olefins.

In order to determine what is unique about hydrocarbon measurements in Houston we need "normal" data sets and a methodology for comparison. These topics are addressed in Sections 2 and 3. Results are presented in Section 4. We compare hydrocarbons in Houston with those measured elsewhere, concentrating on samples collected during similar aircraft flights in Philadelphia and Phoenix. Comparisons are done on the basis of species concentration and OH-reactivity. Maps of the Houston area are used to show locations with high concentrations of individual compounds. Sections 5 and 6 present Conclusions and Recommendations.

2. Data Sets

The primary data set used to characterize the ambient atmosphere in Houston is from the DOE G-1 aircraft. Hydrocarbon samples were collected in 3 liter Summa electropolished canisters and analyzed at York University by GC-FID as described in *Kleinman et al.*, [2003a]. A similar sampling and analysis procedure was used for hydrocarbon canisters collected during field campaigns in Phoenix and Philadelphia (see below). Sample analysis in each field program yields concentrations of about 100 hydrocarbons. We will be considering only anthropogenic components, specifically excluding isoprene, even though there is an industrial source of this compound in Houston. We restrict our attention to samples collected at altitudes below 1000 m msl in Philadelphia and Houston and below 2000 m msl in Phoenix. For most samples this is mid-boundary layer altitude. A higher altitude range is allowed for Phoenix to account for elevated terrain and a higher mixing height in the dry desert. All concentrations are reported in mixing ratio units of ppb by volume of compound.

Approximately 10% of the Houston G-1 samples and a lesser fraction of the Phoenix samples were contaminated because of leaky fittings on the canisters. These samples were initially identified on the basis of very high concentrations of i-pentane, toluene and other compounds [*Kleinman et al.*, 2003b]. Subsequent identification was made on the basis of leak tests. The identified contaminated samples have been removed from further consideration. Any remaining contamination issues are judged to be non-existent or minor.

In order to identify anomalies in Houston one needs to have a definition of what is normal. Possibilities considered included surface measurements from the Washburn Tunnel during TexAQS 2000; surface measurements from U.S. cities between 1984 and 1986 from the 39 City Study; and aircraft measurements that we collected in field campaigns in 4 other metropolitan areas.

2.1 Washburn Tunnel

This data set is the best representation of vehicle emissions in the Houston area [*McGaughey et al.*, 2004]. However, vehicle emissions are only one part of a normal urban hydrocarbon mixture (see Sec. 4.4). Hydrocarbon samples taken in the tunnel are of fresh

emissions, while the ambient measurements taken from aircraft and surface sites have been exposed to varying degrees of atmospheric processing. Figure 1 illustrates the effects of such processing by showing how the reactivity of Washburn Tunnel samples are predicted to change as a function of photochemical age (product of OH concentration and atmospheric residence time). It is seen that reaction with OH reduces total reactivity and changes proportions so that less reactive compounds make a greater percent contribution to older samples. Similar considerations apply to changes in concentration.

2.2 39 City Study

By virtue of making measurements in a wide range of locations this data set could be used as a definition of normal [Seila *et al.*, 1989]. However the measurements were made between 1984 and 1986. Since then there have been emission control regulations that have reduced emission amounts (at least on a per usage basis, i.e. per vehicle mile or can of paint) and also have changed the relative amounts of various hydrocarbons (i.e. reduction of more volatile gasoline ingredients and benzene). The 39 city measurements are taken at relatively polluted surface sites. Comparison with our aircraft measurements will be biased because the air masses that we sampled have been effected by atmospheric processing.

2.3 G-1 data sets from other cities

We have conducted aircraft based photochemistry field campaigns in 5 metropolitan areas; Nashville, TN (1995), New York City, NY (1996), Phoenix, AZ (1998), Philadelphia, PA (1999), and Houston, TX (2000). As described in Kleinman *et al.*, [2002, 2004a], sampling strategies in Phoenix, Philadelphia, and Houston emphasized emission source regions, while sampling in Nashville and New York City was primarily conducted in rural and suburban areas outside of the center city. Table 1 presents an overview of the 3 cities which can be most easily compared; Phoenix, Philadelphia, and Houston. Two values are given for the number of hydrocarbon samples collected in each city. The first, smaller, value, refers to the number of samples for which auxiliary data existed such that a photochemical model could be used to calculate O₃ production rates. It is this data subset that has been used in publications. The second, larger, value includes hydrocarbon samples

which don't have all of the auxiliary data for an O_3 production rate calculation. Unless otherwise indicated that is the data set used in this report.

Figure 2 taken from *Kleinman et al.*, [2004a] shows the location of hydrocarbon samples in the 3 cities relative to the locations of NO_x emissions sources. In TexAQS 2000, about half of the G-1 samples were collected in the Ship Channel region and to the west along urban portions of the I-10 corridor. Although the general focus on sampling near emission sources can be seen from these maps (especially in comparison to maps for Nashville and NYC, not shown), the maps do not provide a quantitative view of similarities and differences in sampling strategies between the 3 cities.

In Figure 3 we show a NO_x frequency distribution for Phoenix, Philadelphia, and Houston which is based on G-1 measurements at the times and locations that hydrocarbon samples were collected. As in Figure 2 we are showing samples from the smaller subset coincident with the photochemical calculations. If we accept NO_x concentration as a general metric of sampling conditions and local pollution levels, either Phoenix or Philadelphia could serve as the norm against which the Texas samples are compared. Support for this viewpoint is found in Figure 4 which shows frequency distributions for acetylene, a long-lived constituent of vehicle exhaust which is often used as a tracer for urban emissions. As with NO_x , the frequency distribution of acetylene is very similar in the 3 cities. In the following sections we will describe ways of taking into account the feature that median NO_x and C_2H_2 in Houston is actually 39% and 34%, respectively, greater than in Philadelphia.

Despite having similar distributions of NO_x and C_2H_2 , the distributions of hydrocarbons in Phoenix, Philadelphia, and Houston are very different. Much of this report is devoted to exploring these differences.

3. Methodology for Comparisons

The challenge that we face is to identify unusual features of the hydrocarbon composition in Houston, given 1) the difficulty of identifying what is normal and 2) the large concentration difference that result from differences in sampling strategies (close to or far away from high emission rate regions), emission rates, and atmospheric dispersion. We will refer to the sum total of these effects on absolute concentration as dilution factors.

Because absolute concentrations are not necessarily indicative of a city's hydrocarbon emissions we are more interested in questions of speciation.

Our definition of a normal hydrocarbon speciation will be that which was observed in Philadelphia, a large urban area, with nearby utilities and industrial sites that contribute but don't overwhelm the urban emissions [*Kleinman et al.*, 2004a,b]. Although Figures 3 and 4 suggest that Phoenix is an equally good yardstick for comparison, data presented below will show that Phoenix has much lower hydrocarbon concentrations than either Philadelphia or Houston.

A way of normalizing out the effect of dilution factors is to take the ratio of a particular compound to a tracer compound. The ideal compound to use as a "normalizing factor" is one that is relatively long lived and is emitted in constant proportion to "normal" urban emissions. We base our normalization on C_2H_2 , which is a long lived ($k_{OH} = 9.1 \times 10^{-13} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$) constituent of vehicle emissions. Over times scales appropriate for same day urban transport, C_2H_2 is nearly inert. Ten hours of exposure to an average OH concentration of $5 \times 10^6 \text{ molec cm}^{-3}$ will reduce C_2H_2 by just 15%. There are, however, acetylene sources in the Ship Channel region which are evident as outliers on a C_2H_2 vs. CO scatter plot (not shown). The number of such outliers is small. Figures 3 and 4 show that inter city differences for NO_x and C_2H_2 are both relatively small and are nearly constant across the whole frequency distribution.

Normalization was done by dividing the concentration of species i by the median concentration of tracer in that city. For compound i in the J^{th} sample, the normalized hydrocarbon concentrations is:

$$HC_J(i)_{\text{NORMALIZED}} = C_J(i)_{\text{CITY}} / C_{\text{Median}}(\text{tracer})_{\text{CITY}} \quad (1)$$

According to (1), the Houston samples are enriched in a particular species if:

$$C_N(i)_{\text{HOU}} > C_N(i)_{\text{PHL}} \times (\text{Median Houston tracer} / \text{Median Philadelphia tracer}) \quad (2)$$

where

N is a percentile value in the hydrocarbon frequency distribution

i identifies a particular compound

$$(\text{Median Houston } \text{C}_2\text{H}_2 / \text{Median Philadelphia } \text{C}_2\text{H}_2) = 1.34 \quad (3)$$

Note that the definition of enrichment is based on an inter-city comparison at a designated point on the hydrocarbon frequency distributions. Medians are useful for comparing typical conditions, while samples near the 90th percentile are useful for comparing the high concentration events that have been linked to high O₃ production rates and O₃ episodes.

Our assessment of what is an anomalous hydrocarbon concentration in Houston will depend of our choice of tracer. We present some results using i-pentane, where

$$(\text{Median Houston i-pentane} / \text{Median Philadelphia i-pentane}) = 1.88 \quad (4)$$

The argument for using i-pentane is that it is usually the most abundant hydrocarbon and it better characterizes vehicle emissions because it is emitted both from the tailpipe and fuel evaporation. However, i-pentane is not inert over time scales of 1 day ($k_{\text{OH}} = 3.9 \times 10^{-12} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$) and it is likely that there are significant industrial sources in Houston from petroleum refineries. Because the i-pentane ratio is greater than the C₂H₂ ratio (compare (3) and (4)), using i-pentane to identify compounds in Houston with anomalously high concentrations, provides a more stringent criteria.

An alternate way of normalizing hydrocarbon concentrations for dilution effects

Instead of using a city's median tracer as a normalization factor, each sample can be normalized by the concentration of tracer in that sample. Then, for compound i in the Jth sample, the normalized hydrocarbon concentrations is:

$$\text{HC}_J(i)_{\text{NORMALIZED}} = \text{C}_J(i) / \text{C}_J(\text{tracer}) \quad (5)$$

This method yields a result for each sample that can be interpreted independently of where that sample lies in a hydrocarbon concentration frequency distribution. The disadvantage of (5) is that it incorporates an extra source of variability due to the circumstance that the tracer is not emitted in a fixed proportion to other species within an ensemble of "normal" urban samples. We have used (1) and (5) to compare Philadelphia and Houston G-1 data sets. In

general, both methods reach the same conclusion as to which compounds are enriched in Houston.

4 Results

4.1 Reactivity

Figure 5 compares anthropogenic hydrocarbon reactivity in the 3 cities, defined by

$$\text{Reactivity} = \sum k_i [\text{HC}(i)] \quad (6)$$

where k_i is the rate constant (298 °K, 1 atm) for reaction of HC(i) with OH radical. The sum is over all quantified hydrocarbons, the set of which did not vary significantly in the 3 field campaigns. Two dotted lines have been added to Figure 5 to show Philadelphia reactivity increased by factors of 1.34 and 1.88 representing ratios of C_2H_2 and i-pentane in these 2 cities. A comparison of the Houston data with the normalized Philadelphia data thereby takes into account the possibility that sampling in Houston was more source oriented than in Philadelphia.

Reactivity in Phoenix is seen to be about a factor of 2 to 3 lower than in Philadelphia, a difference that can't be explained by a less source-oriented sampling strategy in Phoenix. Figure 2 shows that median NO_x concentrations in Phoenix and Philadelphia are nearly identical; the hydrocarbon tracer ratios are both less than the factor of 2 to 3 which separates Phoenix and Philadelphia reactivities:

$$(\text{Median Philadelphia } \text{C}_2\text{H}_2 / \text{Median Phoenix } \text{C}_2\text{H}_2) = 0.93$$

$$(\text{Median Philadelphia i-pentane} / \text{Median Phoenix i-pentane}) = 1.5 \quad (7)$$

Reactivity in Houston is greater than in Philadelphia for samples above the 30th percentile. The difference between these two cities starts out small (< factor of 2) until above the 90th percentile at which point the Houston anthropogenic hydrocarbon reactivity becomes several-fold greater than Philadelphia. As this is the high end of the distribution, the absolute differences between these 2 cities becomes very large. Thus, the highest reactivity observed in Philadelphia and Houston are 11 s^{-1} and 47 s^{-1} , respectively. This

difference has been attributed mainly to light olefins from petrochemical facilities. Normalizing the Philadelphia data decreases the differences between it and Houston. With C_2H_2 as a normalizing factor, Houston reactivity is greater than Philadelphia above the median; with i-pentane, Houston's higher reactivity only occurs above the 90th percentile.

In Figure 6 we compare reactivity by classes of compounds, with the light C_2 - C_4 olefins separately displayed. The 5 panels on this graph correspond to 5 deciles in reactivity, ranging from > 90% to 50-60%. For all 5 deciles the reactivity ordering is Houston > Philadelphia > Phoenix. Because the NO_x concentrations in these 5 cities are similar this implies that the hydrocarbon/ NO_x ratio is also ordered the same way. Normalization corrections have not been applied to Figure 6. Doing so, will reduce the differences between Philadelphia and Houston, but with a normalization factor of 1.34 based on C_2H_2 , the ordering is preserved.

While it is true that the largest difference, both in an absolute and relative sense, appear at the top of the frequency distribution (in the most polluted samples), the difference persist in all 5 deciles presented in Figure 6. As can be seen from the speciation, the major differences, in an absolute sense, between Houston and Philadelphia are due to ethylene, propylene, and to a lesser extent butenes. In a relative sense, Houston has a light alkane reactivity that is about a factor of 2 greater than Philadelphia. Phoenix has a much lower reactivity in all categories except for aromatic compounds in the top 3 deciles. The cause for this very low reactivity in Phoenix is not known. Judging from surface measurements and photochemical age calculations [Kleinman *et al.*, 2003a], it is not due to a more photochemically aged mixture in Phoenix compared with the other cities. We return to this point as a recommendation for further study.

Figures 7-9 show an inter-city reactivity comparison by deciles for light alkanes, butenes, and aromatics, respectively. Light alkanes contribute 9-25% to the hydrocarbon reactivity in Houston (smaller percent in more reactive samples). In absolute value their contribution is 2.2 to 2.5 times greater than in Philadelphia. The most significant compounds in this category from a reactivity standpoint are i-butane and i-pentane. Ethane concentrations in Houston are more than twice that in Philadelphia, but the contribution to reactivity is minimal.

According to Figure 8, the excess butene reactivity in Houston relative to Philadelphia is due mainly to 1,3 butadiene and 1-butene. i-butene is also a large reactivity contributor but concentrations in Houston and Philadelphia are comparable. Figure 9 indicates that city to city differences for 6 common aromatic compounds are relatively minor compared with other classes of compounds. Additional aromatic compounds are included in Figure 6, which cause aromatic reactivity for some deciles in Philadelphia to be greater than in Houston.

Ethylene and propylene are identified in Figure 6 as major contributors to hydrocarbon reactivity in Houston. The box plot graphs (Figures 10a and 11a) establish the fact that it is an unusual occurrence in Phoenix and Philadelphia for 20% of the anthropogenic hydrocarbon reactivity to be due to either ethylene and propylene. Yet this occurs frequently in Houston. We have split the data set into reactivity bins showing that samples with high percent ethylene occur in concentrated – high reactivity cases and dilute – low reactivity cases. Samples with >20% reactivity from propylene occur mainly in high concentration cases. Figure 10b and 11b show the geographic distribution of samples with more than 20% reactivity from ethylene and propylene. The red dots representing high reactivity samples ($k > 5 \text{ s}^{-1}$) are concentrated near emission sources on the ship channel. Samples indicated with yellow dots have lower reactivity ($k < 5 \text{ s}^{-1}$) but also have a high percentage of ethylene and propylene. Figure 10b shows a halo of yellow dots around the Houston metropolitan area due to the transport of industrial ethylene emissions away from the source regions. The propylene halo (Figure 11b) is not as extended as that for ethylene, presumably because reaction with OH (3 times faster than ethylene) discourages long transport distances.

4.2 Concentration

Table 2 gives the median and 90th percentile value for 26 common hydrocarbons compounds in Phoenix, Philadelphia, and Houston. Compounds are arranged by structure: C_2H_2 , alkanes, olefins, and aromatics. The list is based on the 25 most abundant species in the 39 city study [Chameides *et al.*, 1992] except for the addition of styrene and 1,3

butadiene, the separate quantification of 1-butene and i-butene, and the absence of 1,2,4 tri-methylbenzene and 2,2,4 tri-methyl pentane which were not quantified in all 3 cities.

The following 2 Tables present a comparison between Philadelphia and Houston G-1 hydrocarbon samples for median values (Table 3) and for the 90th percentile values (Table 4). Each Table presents the unadjusted concentration ratios, then the ratios normalized according to (1) using C₂H₂ and i-pentane as tracers. In both Tables 3 and 4, compounds are listed in descending order according to the Houston to Philadelphia concentration ratio. Table entries in which the normalized ratios are greater than 1 have been shaded. The larger the value, the more that compound is enriched in Houston and the greater the statistical significance of that result. At the median level of the frequency distribution, compounds that are enriched in Houston include C₂-C₆ alkanes, ethylene, propylene, and a few aromatics. The enrichment of the light olefins is confined to ethylene (2.2) and propylene (1.6). With a normalization based on i-pentane, the list of significantly enriched compounds includes only i-butane, ethylene, and propane. At the 90th percentile level, 1,3 butadiene and 1-butene are added to the list of species enriched in Houston. Four of the 5 highest enrichment values are for light olefins; 1,3-butadiene (5.7); propylene (3.5), 1-butene (3.5), and ethylene (3.3). The remaining compounds with enrichment factors above 1.5 are i-butane (3.4), benzene (2.0), ethane (1.8), i-pentane (1.8), n-pentane (1.6), and n-hexane (1.6). All of these compounds are predicted to be enriched on the basis of i-pentane as a tracer, but by lesser amounts.

Frequency distributions for 19 selected compounds are given in Figures 12a to 30a. The concentration range in each graph spans 4 orders of magnitude but the concentration limits differ from graph to graph. A cursory examination shows that some compounds are much more variable than others; i.e., compare propylene with ethane. This feature is linked to atmospheric lifetime as first shown by *Junge* [1974] and applied to hydrocarbons by *Jobson et al.*, [1998]. Many of the frequency distributions can be fit over most of their range by a straight line indicating a log normal distribution of concentrations (Figure 31). For ethylene and propylene the distributions deviates from log normal only at low concentrations and for a few high concentration samples. Because the constituent hydrocarbons have distributions close to log normal, so also does total anthropogenic

reactivity (see Figure 5 and 31c). It appears that the entire Houston area is statistically a single entity for many compounds. This is contrary to the expectation that Houston consists of spatially separated industrial and urban areas, each with their own distinctive properties.

Maps are used to identify locations of high concentration Houston samples. The standard for what is "high concentration" is taken from the Philadelphia data set. Yellow dots are used to identify Houston samples with a concentration above the 97th percentile value for Philadelphia. There are 4 such samples in the Philadelphia data set. The Houston data set is larger, so 6 samples are above the 97th percentile concentration. Red dots are used to identify locations where samples had at least twice the Philadelphia 97th percentile values. If the number of yellow data points is significantly greater than 6, then the Houston data set for that compound has appreciably more high concentration samples than Philadelphia, assuming that sampling conditions in Houston and Philadelphia allow a one to one comparison to be made (see below). The caption under each graph indicates the concentration of the 97th percentile in the Philadelphia data set (and twice this concentrations) as well as the number of Houston samples exceeding these limits. Our use of the 97th percentile Philadelphia sample as defining high concentration is somewhat arbitrary but it appears to work. These samples have a high enough concentration to be regarded as unusual in Philadelphia but are not affected by a small number of Philadelphia outliers.

Results are summarized in Table 5. Compounds are listed in descending order of the number of Houston samples with concentration greater than the Philadelphia 97th percentile. We have to define a cut-off value for the number of occurrences above which we conclude that there is an excess number of high concentration samples in Houston. Again, we rely on C₂H₂. There are 16 high concentration C₂H₂ samples, of which 5-7 have an industrial signature as judged by a lower than expected CO concentration. Removing these samples would give about 10 high concentration acetylene cases. Compounds with a greater number of high concentration samples are identified as having excess occurrences. The list consists of acetylene, light alkanes (ethane, propane, i- and n-butane, i- and n-pentane, and n-hexane), olefins (ethylene, propylene, 1-butene, and 1,3-butadiene), and benzene. There may be additional compounds outside of the of 19 included in this analysis. i-butene is not on

our list because it's 97th percentile concentration is high in Philadelphia. One could question whether there is something anomalous about this compound in Philadelphia. Such questions could of course be applied to the entire Philadelphia data. Barring extensive sampling in more urban areas, there is no absolute way of defining normal.

Most of the figures indicate that high concentration samples are clustered near the Ship Channel with a significant fraction spread out over other areas. Some of these areas appear on multiple maps (i.e. the region on the SW of the city near 29.5, 95.6). Other hot spot are north of Texas City and along the urban part of the I-95 corridor. Our identification of hot spots is of course limited by our spatial coverage and the particular meteorological conditions that were in place when the sampling was done. The highest concentration of points and therefore the greatest statistical significance should be attached to the samples collected along industrial and urban portions of the I-10 corridor.

4.3 Anomalous i-butane to n-butane ratio

We have already noted that Houston has high concentrations of i-butane compared with other cities. This causes the ratio of i-butane to n-butane to be a factor of 2 greater than observed elsewhere. This ratio varies little from city to city so a factor of 2 departure indicates an unusual source contribution. *Parrish et al.*, [1998] present 10 data sets with an average median ratio of 0.48 ± 0.02 1 σ confidence level. Figure 31 shows that the Phoenix and Philadelphia ratios are also about 0.5, but 3 data sets from Houston all give ratios close to 1. *Jobson et al.*, [1998] analyzed hydrocarbon measurements collected in the western Atlantic, the Azores, Boulder CO, and Alert, Canada. They found that the i to n-butane ratio is again about 0.5 with the exception of a site on Sable Island with a ratio of 0.91. This non-urban signature was attributed to a petroleum source, either from a natural seep or a nearby oil production platform.

4.4 Vehicle emissions of light alkanes

Light alkanes with up to 5 or 6 carbon atoms are significantly enriched in the Houston ambient atmosphere compared with vehicle emissions samples in the Washburn Tunnel (Figure 32). The enrichment is particularly large for C₂ to C₄ alkanes and exists also

for Phoenix and Philadelphia (not shown) indicating that the primary source of these compounds is not from motor vehicles.

5. Conclusions

We have compared the Houston G-1 hydrocarbon data set with similar data sets collected in Philadelphia and Phoenix. In these cities the frequency distributions for NO_x and C_2H_2 (a tracer of typical vehicle dominated urban emissions) are nearly identical suggesting that sampling conditions were sufficiently similar to allow a direct comparison with only a small correction factor for the slightly higher C_2H_2 in Houston. Hydrocarbon reactivity in Houston is greater than in Philadelphia, which in turn is greater than Phoenix. The difference between Houston and Philadelphia is primarily due to very high concentrations of light olefins (ethylene, propylene, 1-butene and 1,3 butadiene). A comparison of the most reactive samples in the 3 cities shows that the Houston samples have much higher absolute reactivities than elsewhere and that this difference is about 90% due to the light olefins identified above. Although these samples stand out as being qualitatively different we present evidence that ethylene and propylene are significantly elevated in at least half of the Houston samples. While the very highest concentrations are found near the Ship Channel, samples with an elevated concentration of propylene and especially ethylene are geographically widespread.

Other compounds identified as being significantly enriched in Houston include $\text{C}_2 - \text{C}_5$ alkanes, n-hexane, and benzene, the exact list depending on the method of identification. Reducing the concentrations of $\text{C}_2 - \text{C}_6$ alkanes and benzene back to "normal" urban levels (i.e. $1.34 \times$ Philadelphia values) will reduce the reactivity of the most reactive samples (top decile) by 6%. A similar change applied to the 4 lower deciles will reduce Houston reactivity by 13% to 21%.

- It is an infrequent occurrence in the Philadelphia or Phoenix G-1 data sets to have ethylene or propylene make up 20% of total reactivity. In Houston 36% of the samples exceed the 20% threshold for ethylene and 24% for propylene. Olefins contribute 82% of the anthropogenic reactivity in the most reactive Houston samples (top decile).

- High reactivity samples ($k > 5 \text{ s}^{-1}$) with a high percent contribution from ethylene or propylene are concentrated near the Ship Channel. Samples with lower reactivity ($k < 5 \text{ s}^{-1}$) but with a high percent contribution from ethylene are found throughout the metropolitan area. The high propylene samples are less spread out.
- The i-butane/n-butane ratio in Houston is twice that which has been observed in several different urban areas. Most of this difference is due to elevated i-butane.
- Compounds that are significantly enriched (greater than 50% after normalization with C_2H_2) in Houston relative to Philadelphia at the median of their frequency distribution (i.e. for typical samples) in descending order of enrichment are i-butane (3.2), ethylene (2.2), propane (1.9), n-butane (1.6), n-hexane (1.6), ethane (1.6), and propylene (1.6). Enrichment factors taken from Table 3.
- Compounds that are significantly enriched (greater than 50% after normalization with C_2H_2) in Houston relative to Philadelphia at the 90th percentile level (i.e. for high reactivity samples) in descending order of enrichment are 1,3-butadiene (5.7), propylene (3.5), 1-butene (3.5), i-butane (3.4), ethylene (3.3), benzene (2.0), ethane (1.8), i-pentane (1.8), n-pentane (1.6), and n-hexane (1.6). Enrichment factors taken from Table 4.
- Compounds with very high concentrations, appearing in an excess number of samples (10 or more occurrences), have been identified, using the 97th percentile Philadelphia concentrations as a yardstick. In descending order of the number of occurrences these compounds are: ethane, i-butane, ethylene, propylene, benzene, 1-butene, 1,3-butadiene, n-pentane, i-pentane, n-hexane, n-butane, propane and acetylene.
- The frequency distributions for hydrocarbon reactivity and for the concentrations of many species, including ethylene and propylene, are nearly log normal. There is evidently extensive mixing between emissions from urban and industrial areas so that the final ensemble of measurements appears to be a single statistical entity.

6. Recommendations

- Identify the sources of the light olefins which are apparent in the TexAQS data sets, but under-represented in emission inventories.
- Identify the sources for light alkanes and benzene (compounds towards the top of Tables 3 to 5) which are significantly enriched compared with the Philadelphia (and Phoenix) data sets.
- Use emission based CTMs to determine the relations between a species contribution to hydrocarbon reactivity and its effect on ambient O₃ concentration.
- Find out why the anthropogenic HC/NO_x ratio in Phoenix is so much lower than in Philadelphia or Houston. Is this a feature that is present in emission inventories and if so what emission categories are contributing? What are the implication for urban hydrocarbon control measures in Houston?
- Investigate the industrial emission rates of i-pentane to determine if it is a suitable tracer for "normal" urban activities.
- Use back trajectories to identify the source regions that contribute to the hydrocarbon hot spots located outside of the Ship Channel region.
- Identify the emission sources that have an i-butane/n-butane ratio a factor of 2 greater than observed elsewhere.

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Table 1 Field programs

City	Dates (m/yy)	# flights	# HC samples for P(O ₃) calculation	# HC samples (total)
Phoenix, AZ	5/98 – 6/98	24	110	135
Philadelphia, PA	7/99 – 8/99	20	131	141
Houston, TX	8/00 – 9/00	18	186	200

Hydrocarbon samples are obtained at altitude below 1000 m msl in Philadelphia and Houston and below 2000 m msl in Phoenix

Table 2. 3 City comparison of median and 90th percentile hydrocarbon concentrations

Hydrocarbon	Median (ppbv)				90th percentile (ppbv)		
	Phoenix	Phil.	Houston		Phoenix	Phil.	Houston
acetylene	0.41	0.38	0.51		1.06	0.84	1.18
ethane	1.25	1.86	3.88		1.68	3.44	8.50
propane	0.43	0.97	2.42		1.28	4.05	6.29
n-butane	0.16	0.39	0.85		0.45	1.70	2.86
i-butane	0.069	0.20	0.87		0.20	0.87	3.92
n-pentane	0.12	0.20	0.38		0.42	0.82	1.76
i-pentane	0.28	0.42	0.79		0.99	1.28	3.09
n-hexane	0.040	0.078	0.17		0.14	0.28	0.59
2-methyl pentane	0.067	0.090	0.17		0.24	0.32	0.50
3-methyl pentane	0.046	0.063	0.11		0.16	0.22	0.33
methy-cyclopentane	0.039	0.034	0.068		0.15	0.14	0.23
n-heptane	0.020	0.033	0.050		0.072	0.12	0.15
2-methyl hexane	0.016	0.029	0.038		0.061	0.093	0.12
3-methyl hexane	0.072	0.038	0.042		0.19	0.11	0.13
ethylene	0.25	0.46	1.34		0.88	1.34	5.84
propylene	0.045	0.12	0.25		0.16	0.51	2.42
1,3-butadiene	0.003	0.004	0.0		0.014	0.021	0.16
1-butene	0.010	0.028	0.029		0.025	0.066	0.31
i-butene	0.023	0.048	0.048		0.065	0.16	0.22
benzene	0.10	0.14	0.22		0.23	0.33	0.87
toluene	0.15	0.22	0.26		0.60	0.74	0.81
styrene	0.0	0.019	0.0		0.028	0.18	0.066
ethyl-benzene	0.023	0.024	0.042		0.087	0.10	0.14
o-xylene	0.020	0.015	0.029		0.093	0.084	0.11
m.p-xylene	0.045	0.056	0.061		0.22	0.26	0.33
m-ethyl toluene	0.0	0.002	0.0		0.024	0.016	0.007

missing values or those below detection limit counted as zero concentration

Table 3 Hydrocarbon ratios, constructed from median values for Philadelphia and Houston

Compound	Houston/Phil.	Normalized by	
	Ratio of medians ^a	C ₂ H ₂ ^b	i-pentane ^c
i-butane	4.35	3.24	2.31
ethylene	2.91	2.17	1.55
propane	2.49	1.86	1.33
n-butane	2.18	1.62	1.16
n-hexane	2.18	1.62	1.16
ethane	2.09	1.55	1.11
propylene	2.08	1.55	1.11
methy-cyclopentane	2.00	1.49	1.06
o-xylene	1.93	1.44	1.03
n-pentane	1.90	1.42	1.01
2-methyl pentane	1.89	1.41	1.00
i-pentane	1.88	1.40	1.00
ethyl-benzene	1.75	1.30	0.93
3-methyl pentane	1.75	1.30	0.93
benzene	1.57	1.17	0.84
n-heptane	1.52	1.13	0.81
acetylene	1.34	1.00	0.71
2-methyl hexane	1.31	0.98	0.70
toluene	1.18	0.88	0.63
3-methyl hexane	1.11	0.82	0.59
m.p-xylene	1.09	0.81	0.58
1-butene	1.04	0.77	0.55
i-butene	1.00	0.75	0.53
styrene	0.00	0.00	0.00
1,3-butadiene	0.00	0.00	0.00
m-ethyl toluene	0.00	0.00	0.00

^a C_{MEDIAN(i)HOU}/C_{MEDIAN(i)PHL}^b C_{MEDIAN(i)HOU}/C_{MEDIAN(i)PHL} / 1.34^b C_{MEDIAN(i)HOU}/C_{MEDIAN(i)PHL} / 1.88

Table 4 Hydrocarbon ratios, constructed from 90th percentile values for Philadelphia and Houston

Compound	Houston/Phil.	Normalized by	
	ratio of 90th % ^a	C ₂ H ₂ ^b	i-pentane ^c
1,3-butadiene	7.62	5.68	4.05
propylene	4.75	3.54	2.52
1-butene	4.70	3.50	2.50
i-butane	4.51	3.36	2.40
ethylene	4.36	3.25	2.32
benzene	2.64	1.96	1.40
ethane	2.47	1.84	1.31
i-pentane	2.41	1.80	1.28
n-pentane	2.15	1.60	1.14
n-hexane	2.11	1.57	1.12
n-butane	1.68	1.25	0.89
methy-cyclopentane	1.64	1.22	0.87
2-methyl pentane	1.56	1.16	0.83
propane	1.55	1.16	0.83
3-methyl pentane	1.50	1.12	0.80
acetylene	1.40	1.05	0.75
ethyl-benzene	1.40	1.04	0.74
i-butene	1.38	1.02	0.73
o-xylene	1.31	0.98	0.70
2-methyl hexane	1.29	0.96	0.69
m.p-xylene	1.27	0.95	0.67
n-heptane	1.25	0.93	0.66
3-methyl hexane	1.18	0.88	0.63
toluene	1.09	0.82	0.58
m-ethyl toluene	0.44	0.33	0.23
styrene	0.37	0.27	0.19

^a C_{90%}(i)_{HOU}/C_{90%}(i)_{PHL}

^b C_{90%}(i)_{HOU}/C_{90%}(i)_{PHL} / 1.34

^b C_{90%}(i)_{HOU}/C_{90%}(i)_{PHL} / 1.88

Table 5. Number of Houston samples with higher concentration than one or two times the 97th percentile in Philadelphia.

Hydrocarbon	Philly 97% (ppbv)	Number higher in Houston	2 × Philly 97% (ppbv)	Number higher in Houston
ethane	4.76	83	9.33	13
i-butane	1.63	73	3.26	31
ethylene	2.33	66	4.66	30
propylene	0.84	51	1.68	31
benzene	0.056	39	1.11	10
1-butene	0.13	35	0.26	23
1,3-butadiene	0.061	30	0.12	20
n-pentane	1.32	29	2.64	8
i-pentane	2.57	28	5.13	8
n-hexane	0.58	21	1.16	4
n-butane	2.91	20	5.82	4
propane	6.63	17	13.3	2
acetylene	1.26	16	2.51	2
m.p-xylene	0.48	8	0.96	2
ethyl-benzene	0.19	6	0.38	1
o-xylene	0.20	4	0.40	1
toluene	1.50	3	2.99	1
styrene	0.28	2	0.56	2
i-butene	1.40	1	2.81	1

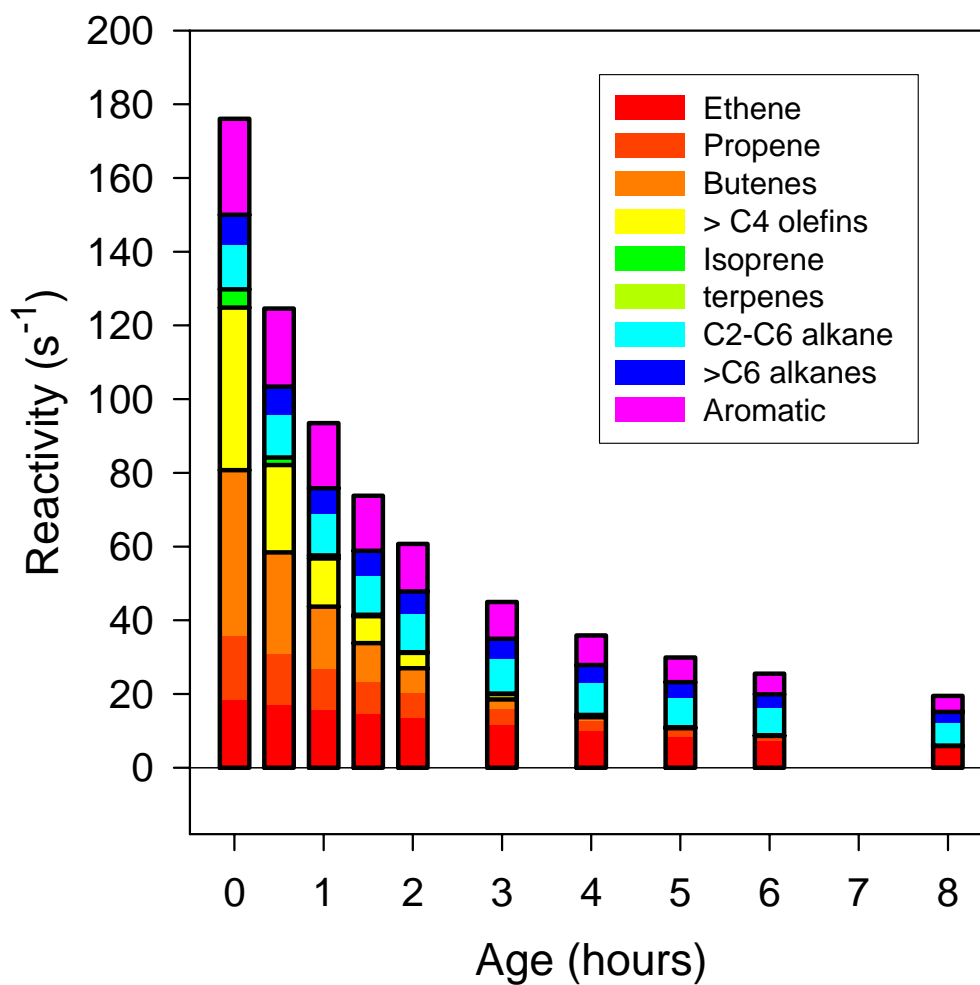
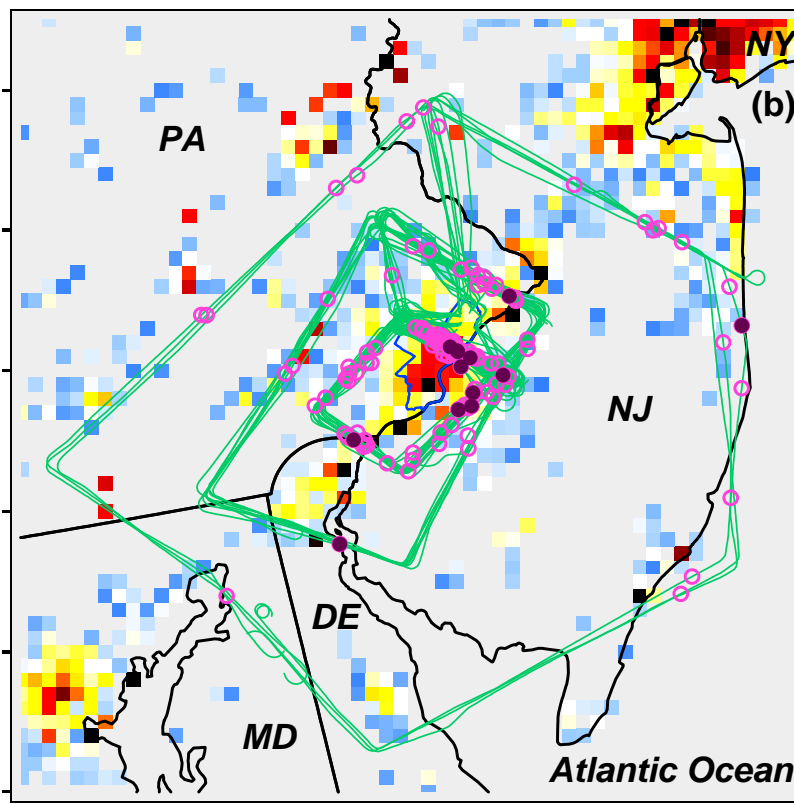
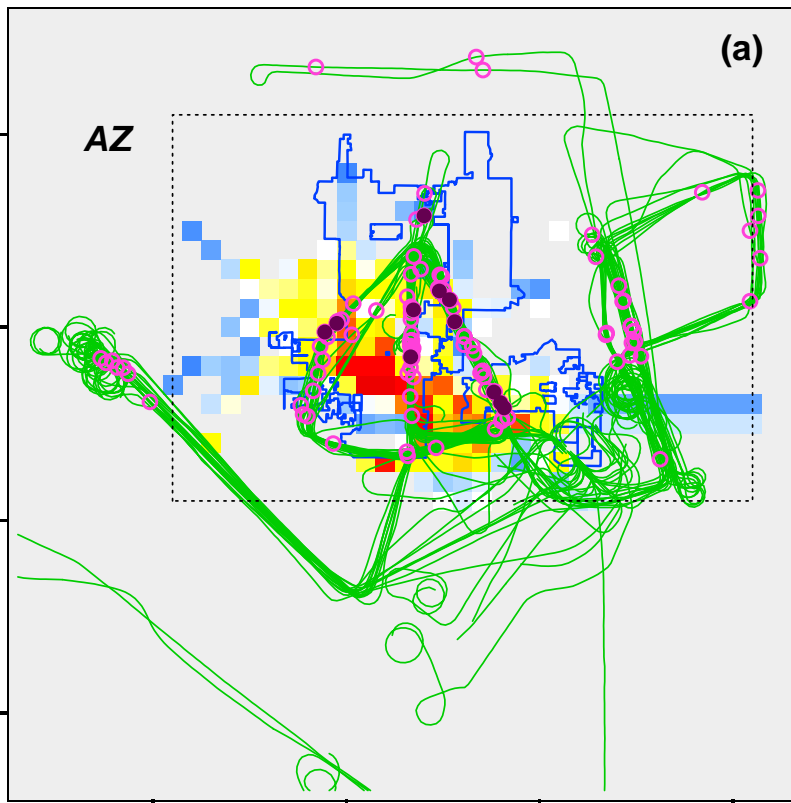


Figure 1 Effect of atmospheric residence time on hydrocarbon reactivity from the Washburn Tunnel samples assuming an OH concentration of 5×10^6 molecules cm⁻³.



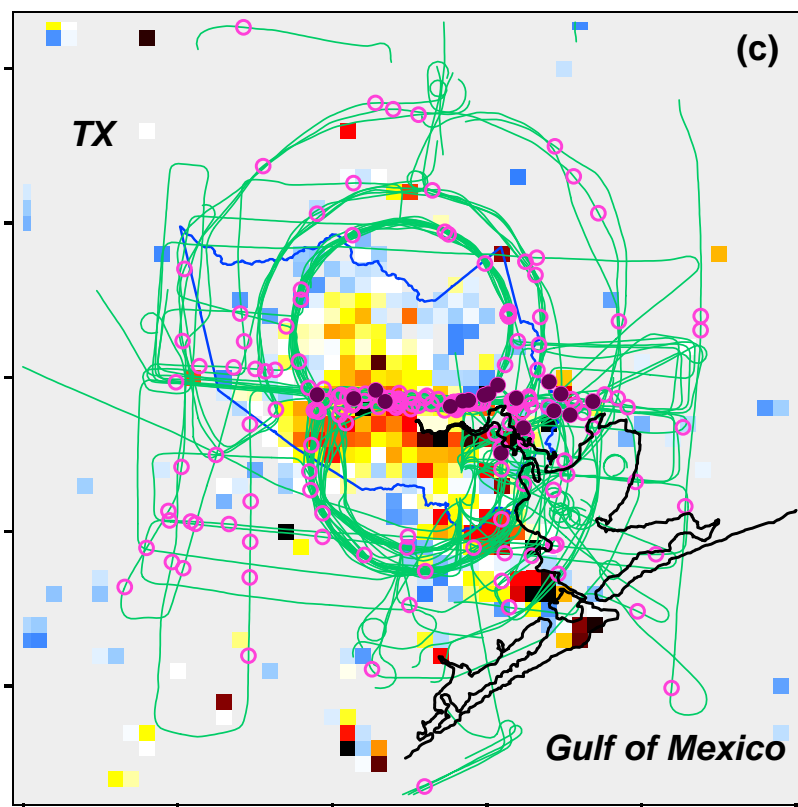


Figure 2. G-1 flight track showing NO_x emission rate and locations of hydrocarbon samples for a) Phoenix, b) Philadelphia, and c) Houston field campaigns. Six samples lie outside the borders of the Texas map. Emission rates are displayed on a log scale in kton/year per 4 by 4km grid cell. Emission data for Nashville, NYC, Philadelphia, and Houston from a Saturday, July 31 18 UTC simulation from the SMOKE model. Phoenix emissions are for a weekday at 18 UTC from a July 1996 inventory compiled by the Arizona Department of Environmental Quality and are limited to the area inside the dashed box in panel (a). The emission scale ranges from 200 to 10,000 ($\log \text{NO}_x = 2.3 - 4$) tons/year with higher rates truncated to 10,000 and lower rates not displayed. State borders are shown in black, city or county borders in blue, and the G-1 ground track for flight segments below 1000 m altitude (2000 m in Phoenix) in green. Open circles indicate locations where hydrocarbon samples were collected and O₃ production rate calculations performed. Darker solid circles indicate calculations that had P(O₃) in the top 10 percentile for that city.

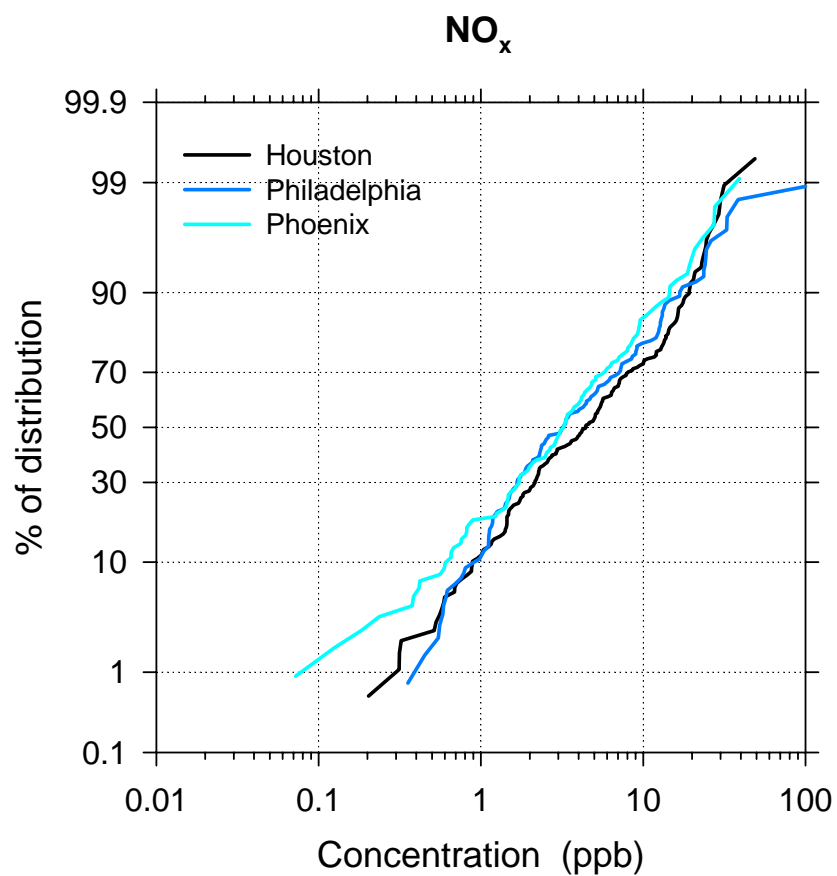


Figure 3. Frequency distribution for NO_x concentration during 3 field campaigns. Data is confined to the times and locations where O₃ production rate calculations were performed. Figure 2 shows locations and Table 1 indicates number of data points and dates for each field campaign.

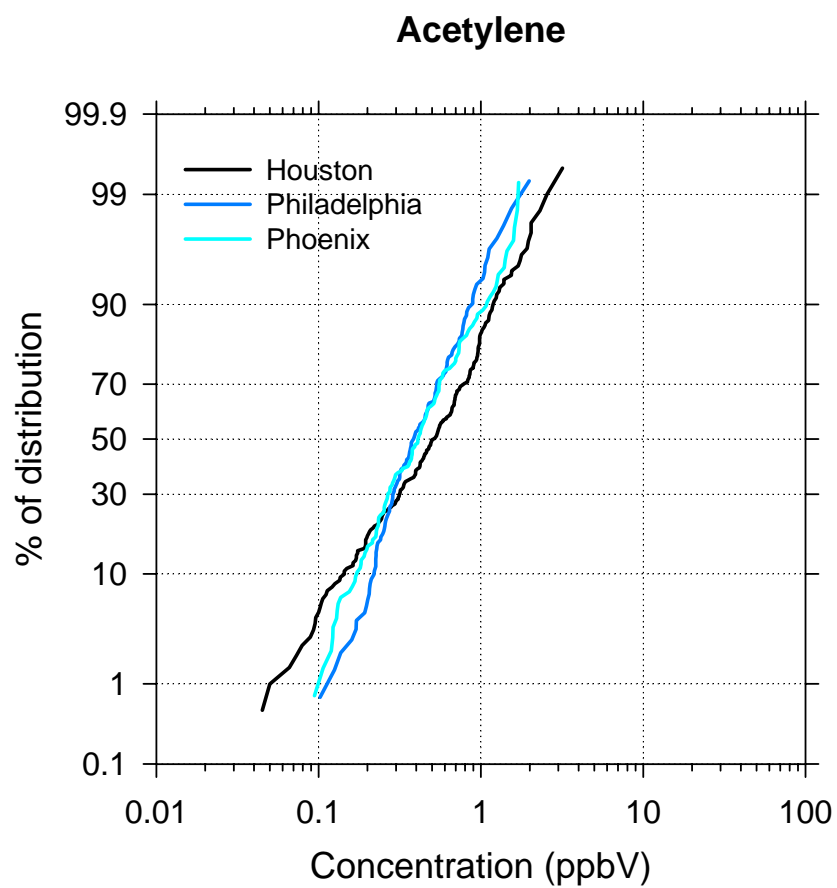


Figure 4. Frequency distribution for C_2H_2 concentration during 3 field campaigns. Full hydrocarbon data set used.

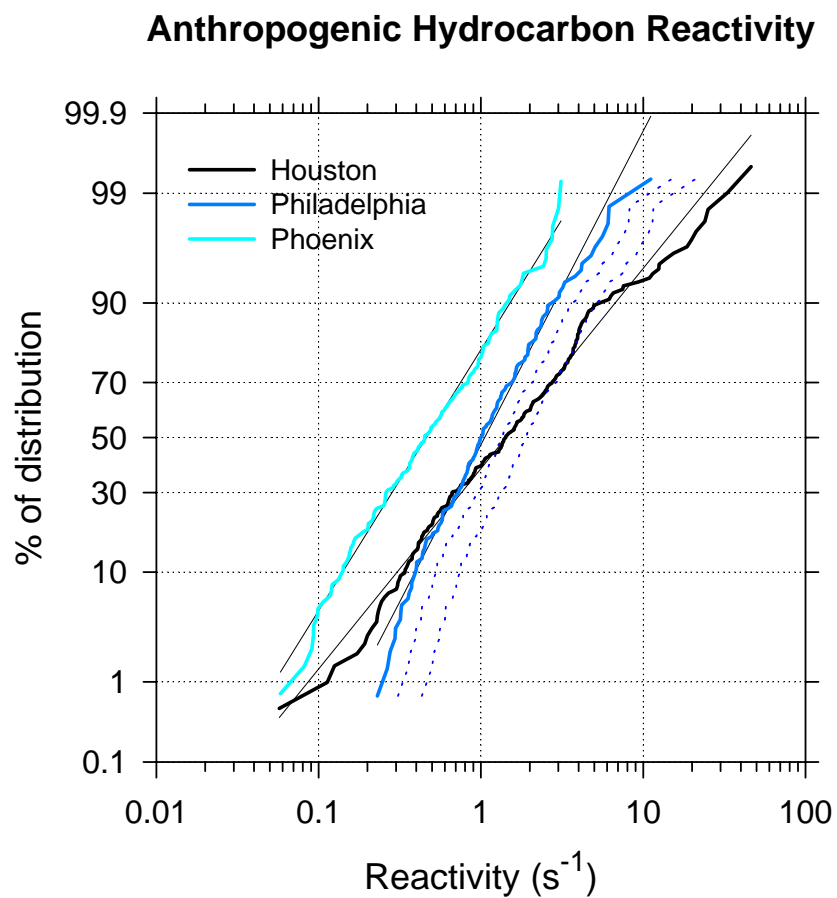


Figure 5. Frequency distribution for anthropogenic OH reactivity during 3 field campaigns. Full hydrocarbon data set used. Thin black lines are a linear least squares fit for each city. Dotted lines show Philadelphia data multiplied by 1.34 or 1.88 to account for higher median concentrations of C_2H_2 and i-pentane, respectively, in Houston.

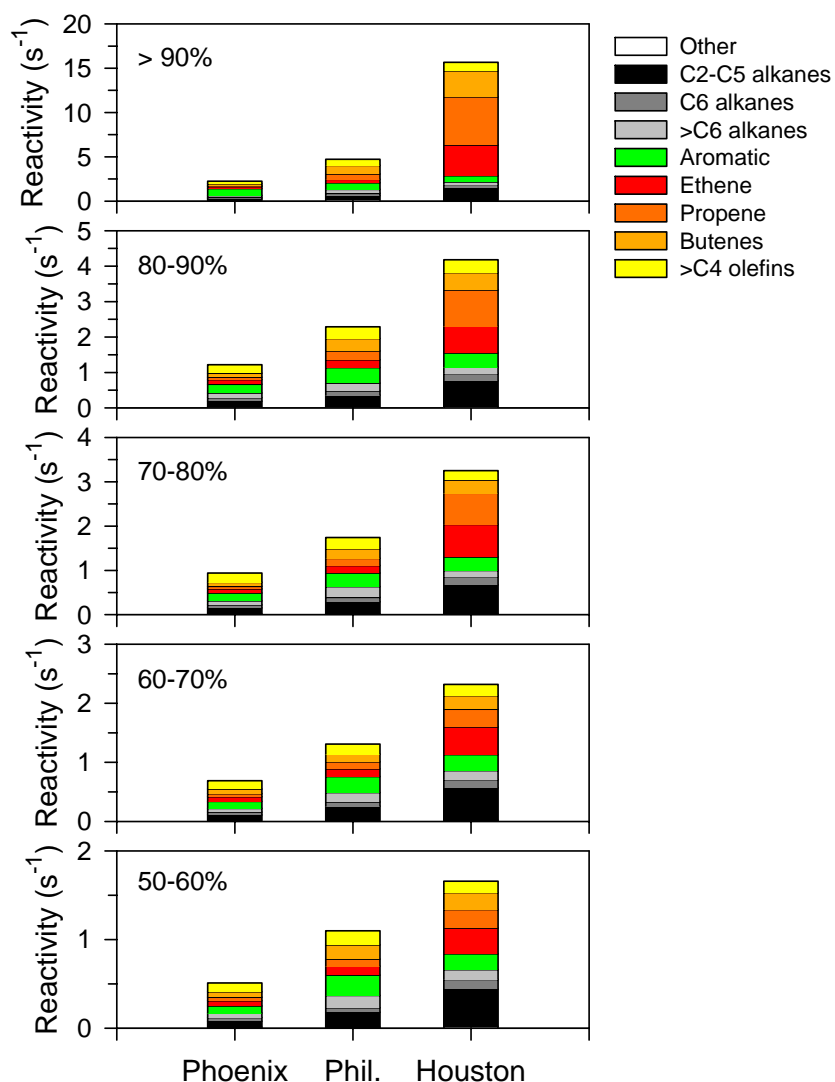
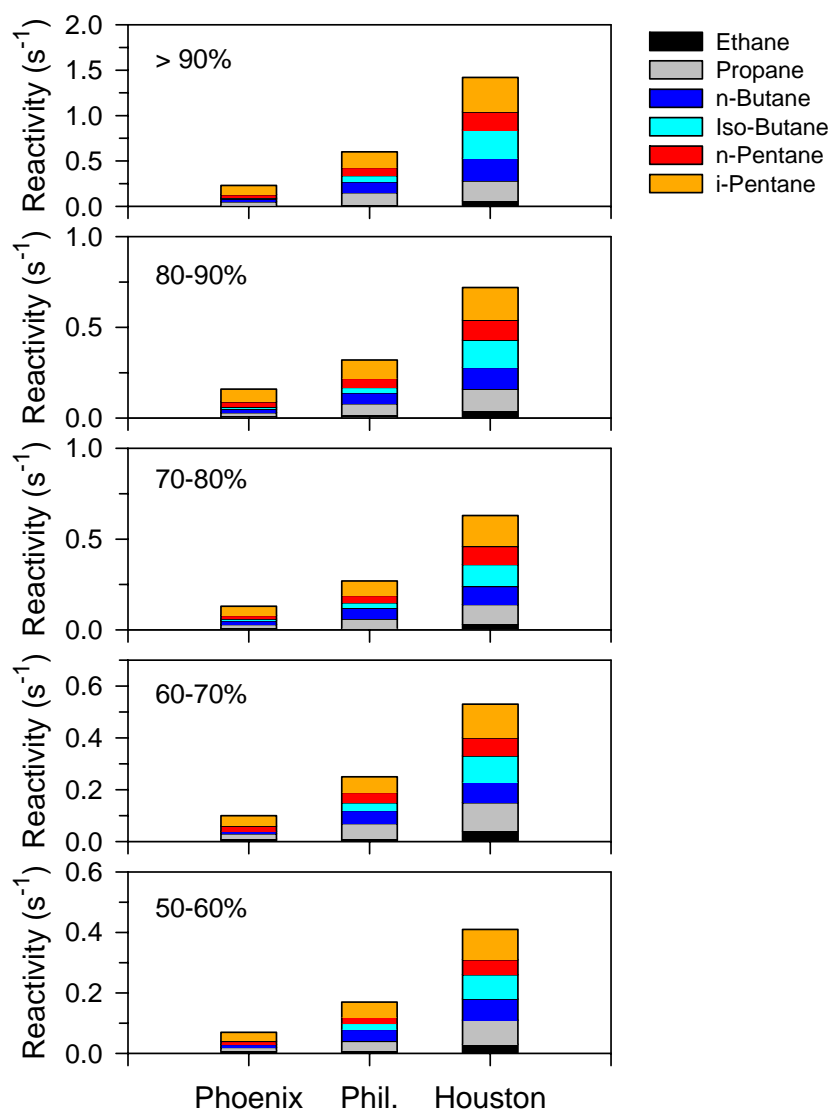
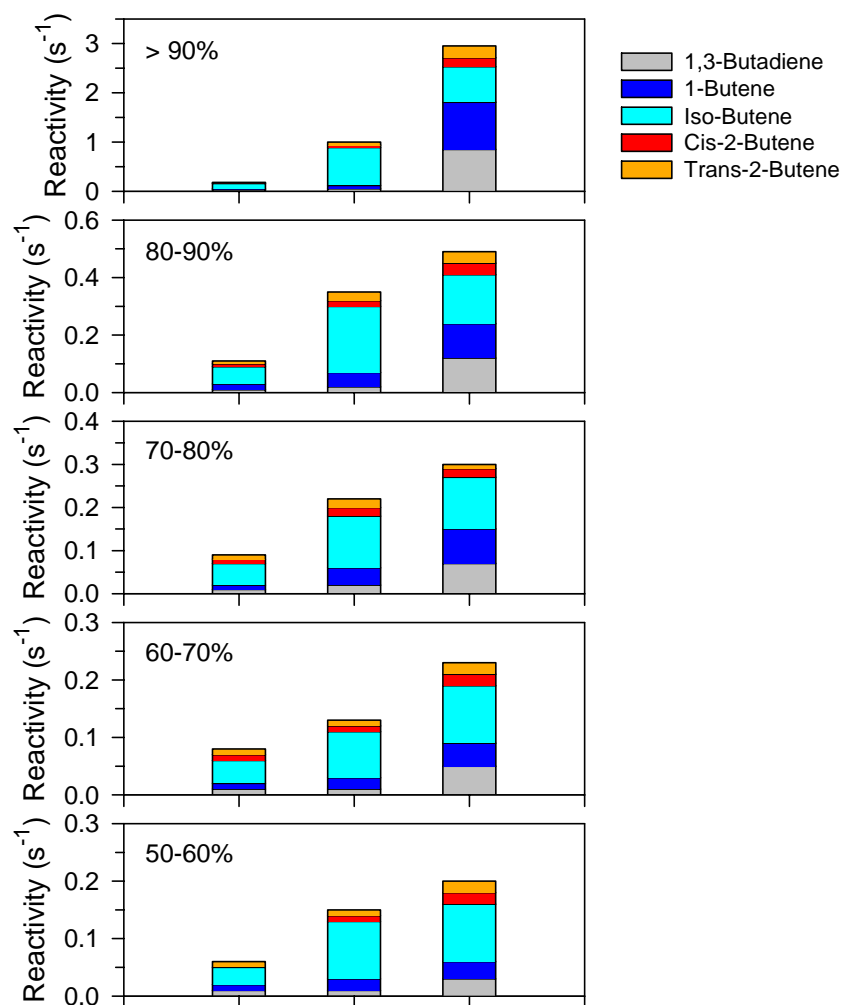


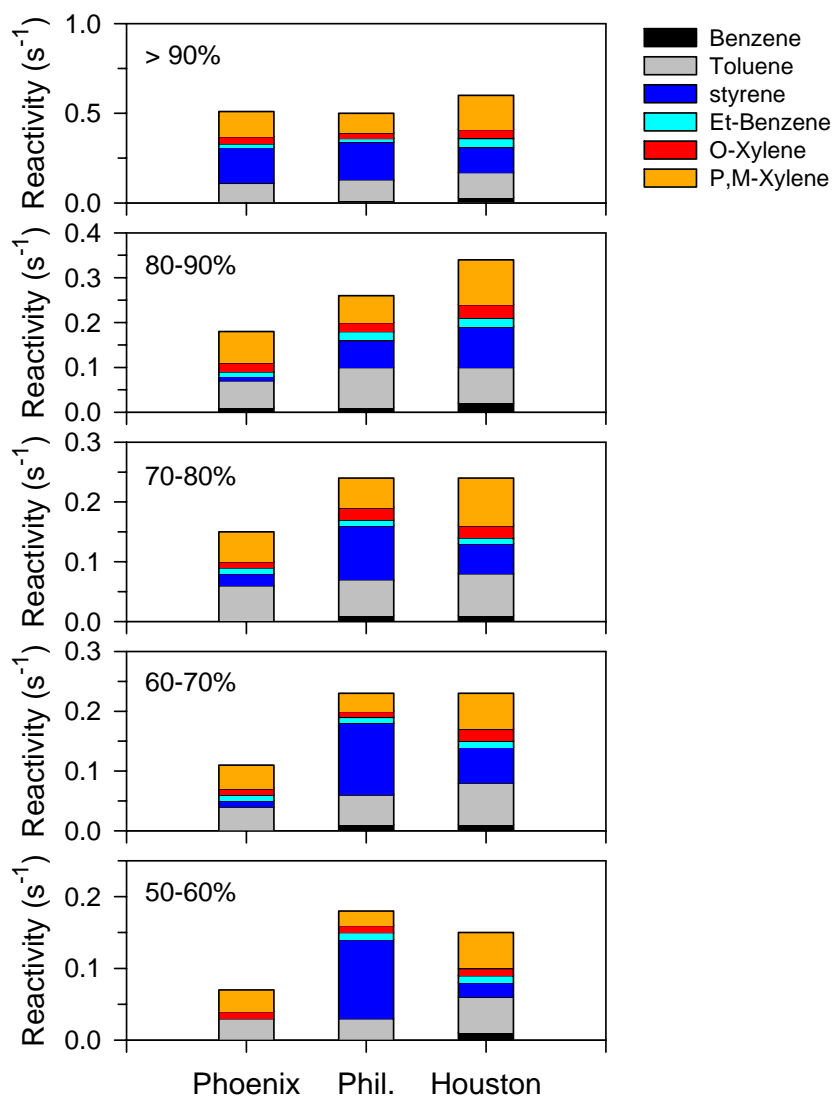
Figure 6. Components of OH – anthropogenic hydrocarbon reactivity for 3 cities. Data subsets have been defined by splitting the anthropogenic reactivity frequency distribution into deciles. For each of the top 5 deciles (i.e. >90%, 80-90%, etc), the component reactivities are determined as an average over samples in that decile. Data has not been normalized.



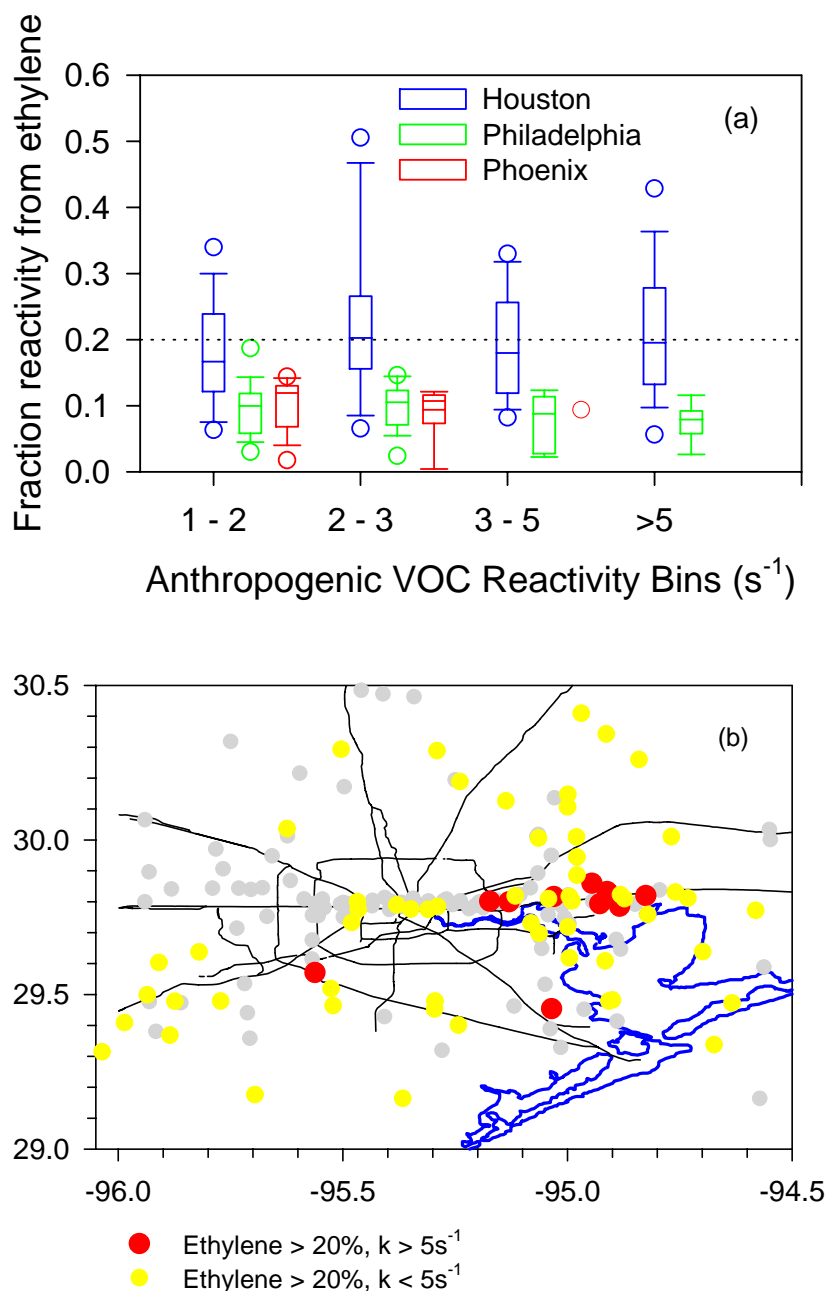
7. Components of light alkane reactivity for 3 cities. Format same as Figure 6.



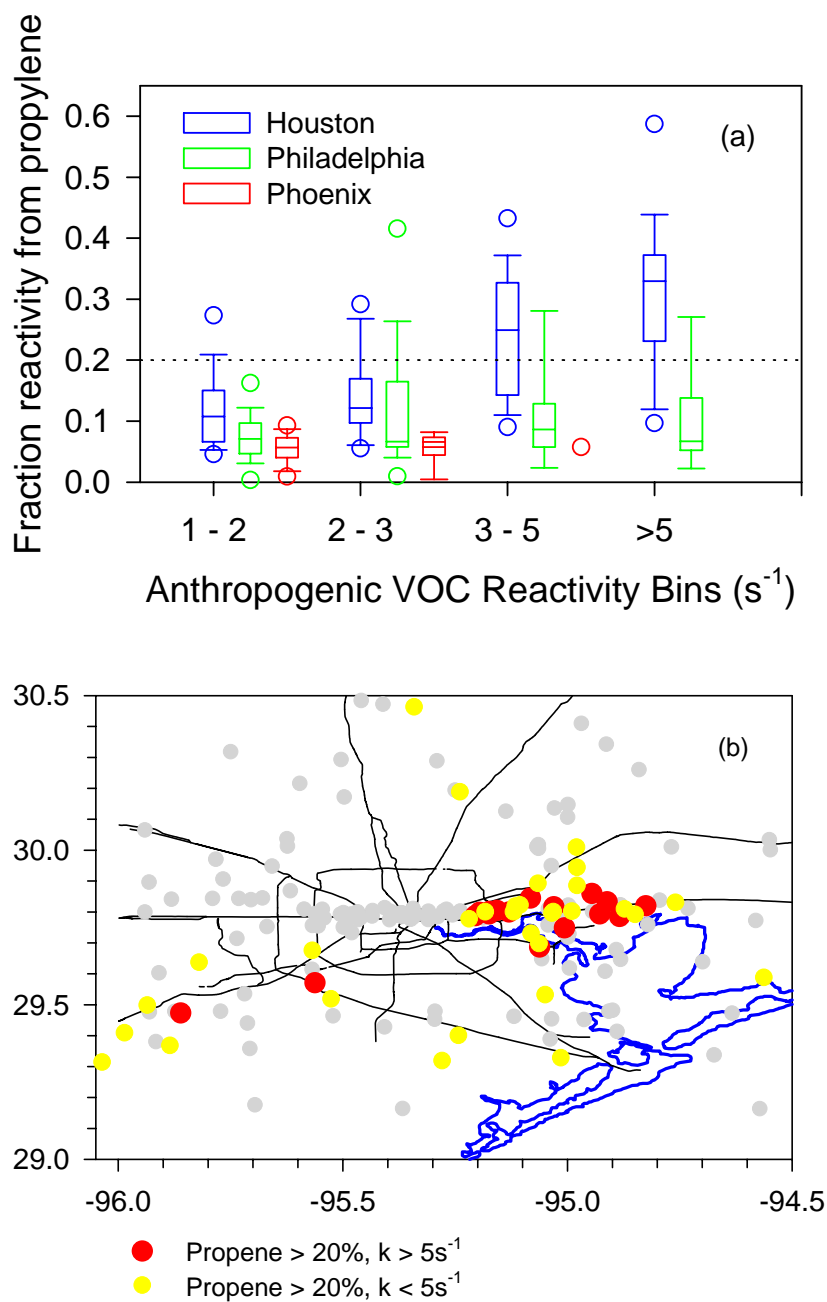
8. Components of reactivity from 4 butene isomers and 1,3 butadiene for 3 cities. Format same as Figure 6.



9. Components of aromatic hydrocarbon reactivity for 3 cities. Format same as Figure 6.



10. (a) Box plot showing percent of anthropogenic reactivity due to ethylene for Phoenix, Philadelphia, and Houston. Data has been divided into 4 reactivity bins. Box shows median value and interquartile range (25th to 75th percentile of distribution). Caps indicate 10th and 90th percentiles; circles indicate the 5th and 95th percentiles. (b) Map of Houston showing locations of hydrocarbons samples (gray filled in circles), identifying those with more than 20% of their reactivity due to ethylene. Data set used in panels (a) and (b) is confined to the times and locations where O_3 production rate calculations were performed.



11 (a) Box plot showing percent of anthropogenic reactivity due to propylene for Phoenix, Philadelphia, and Houston. (b) Map of Houston showing locations of hydrocarbons samples, identifying those with more than 20% of their reactivity due to propylene. Same format as Figure 10.

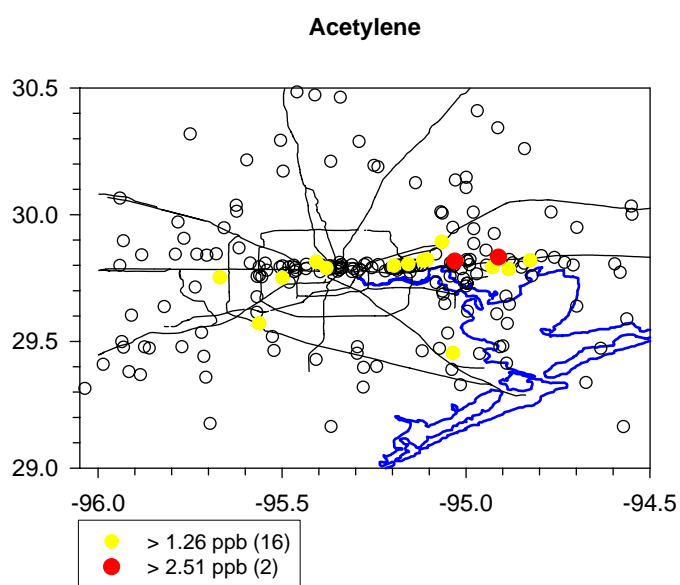
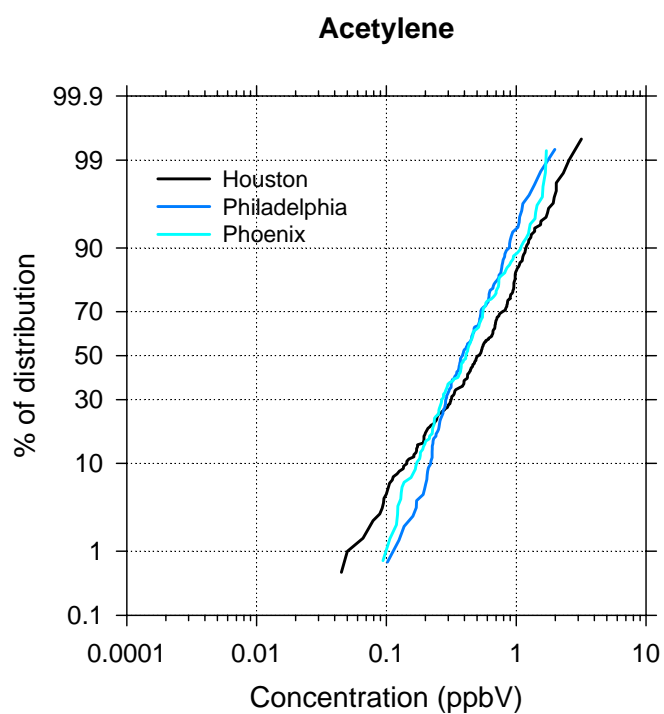


Figure 12 Three city frequency distribution of acetylene concentration with map of the Houston area showing locations of samples with concentrations greater than the 97th percentile in Philadelphia (yellow dots) and greater than twice the 97th percentile (red dots). Numbers of high concentration samples in parenthesis. These numbers appear in Table 5.

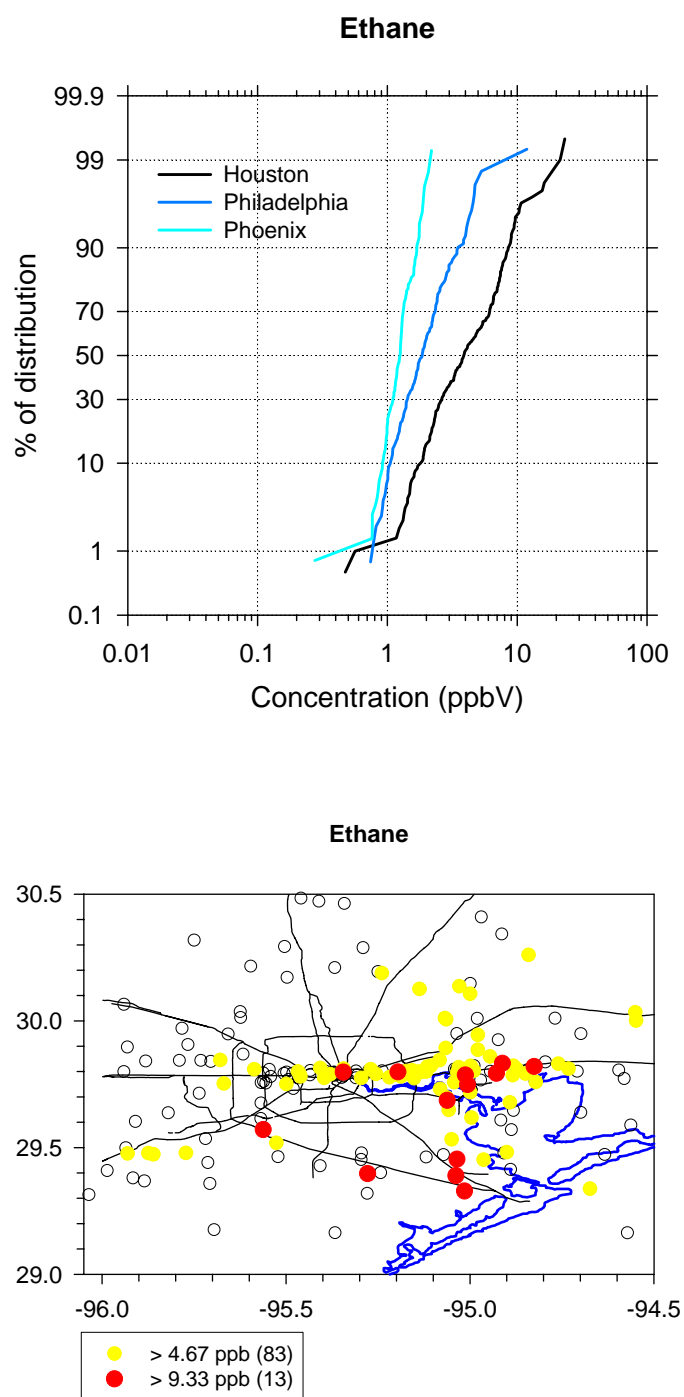


Figure 13 Frequency distribution and map for ethane. Same format as Figure 12.

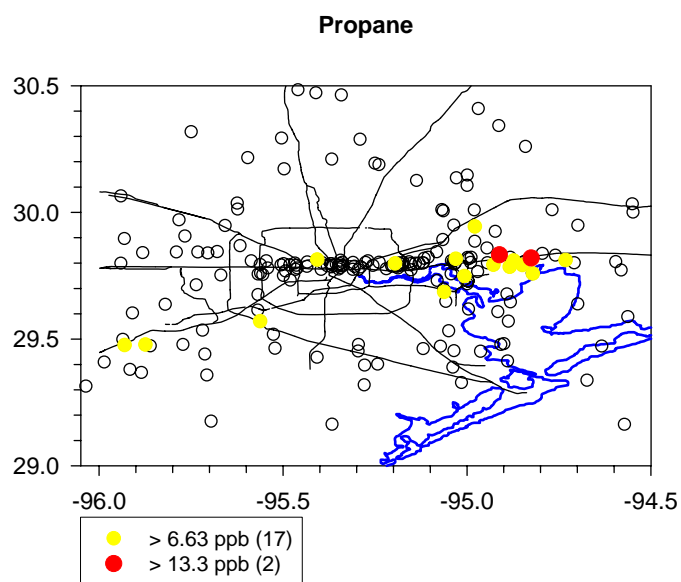
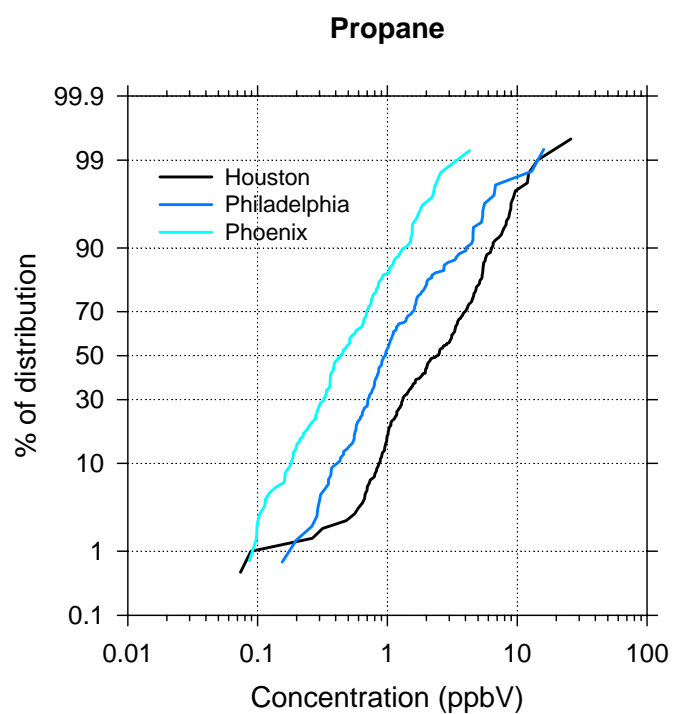


Figure 14 Frequency distribution and map for propane. Same format as Figure 12.

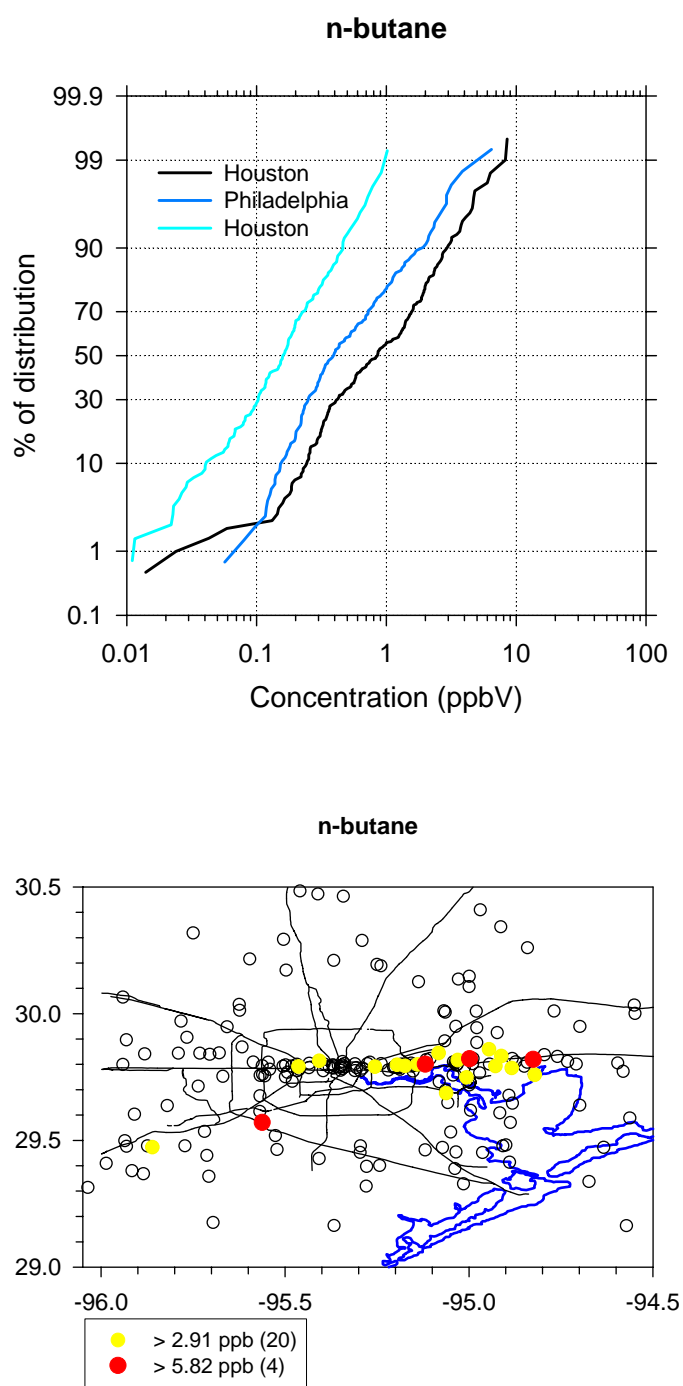


Figure 15 Frequency distribution and map for n-butane. Same format as Figure 12.

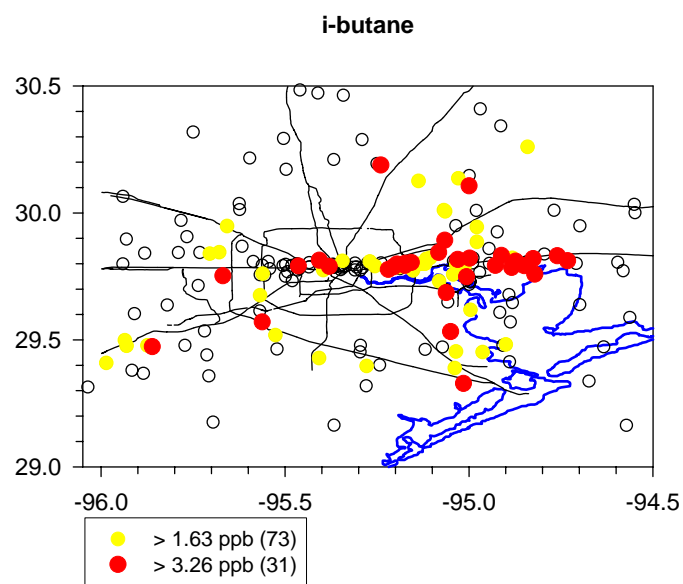
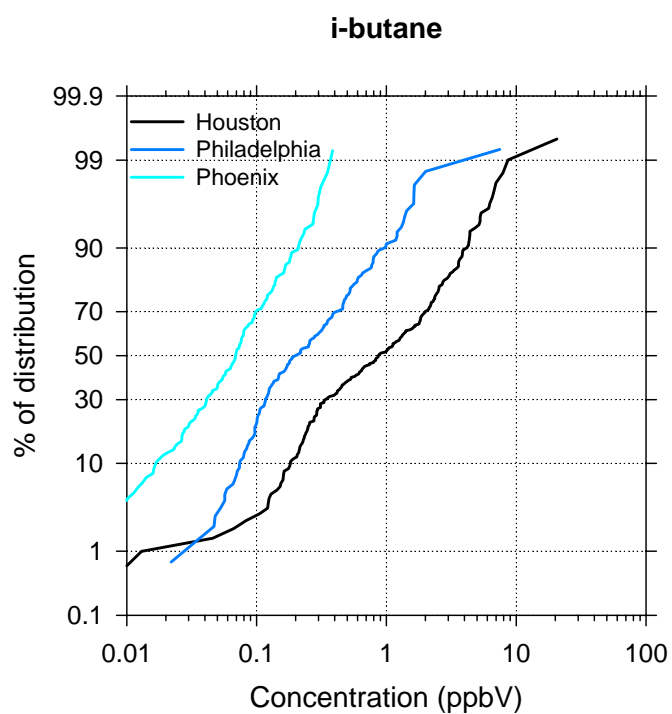


Figure 16 Frequency distribution and map for i-butane. Same format as Figure 12.

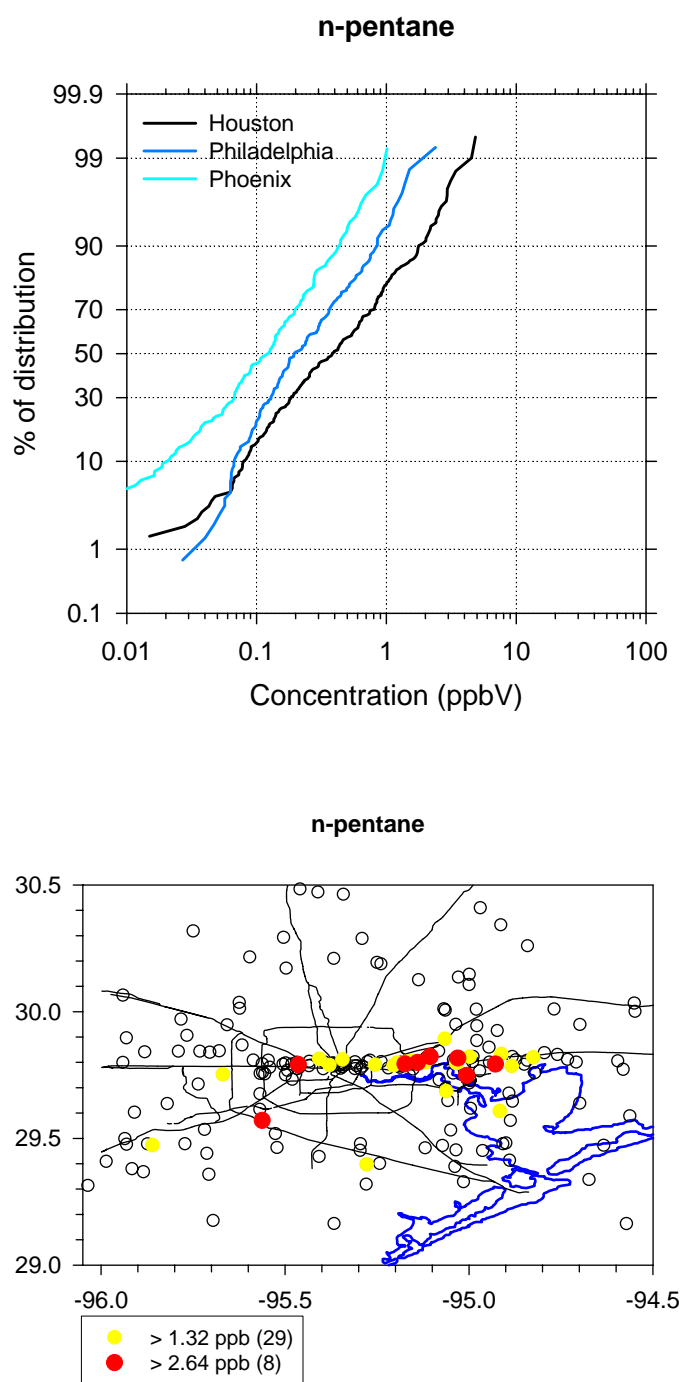


Figure 17 Frequency distribution and map for n-pentane. Same format as Figure 12.

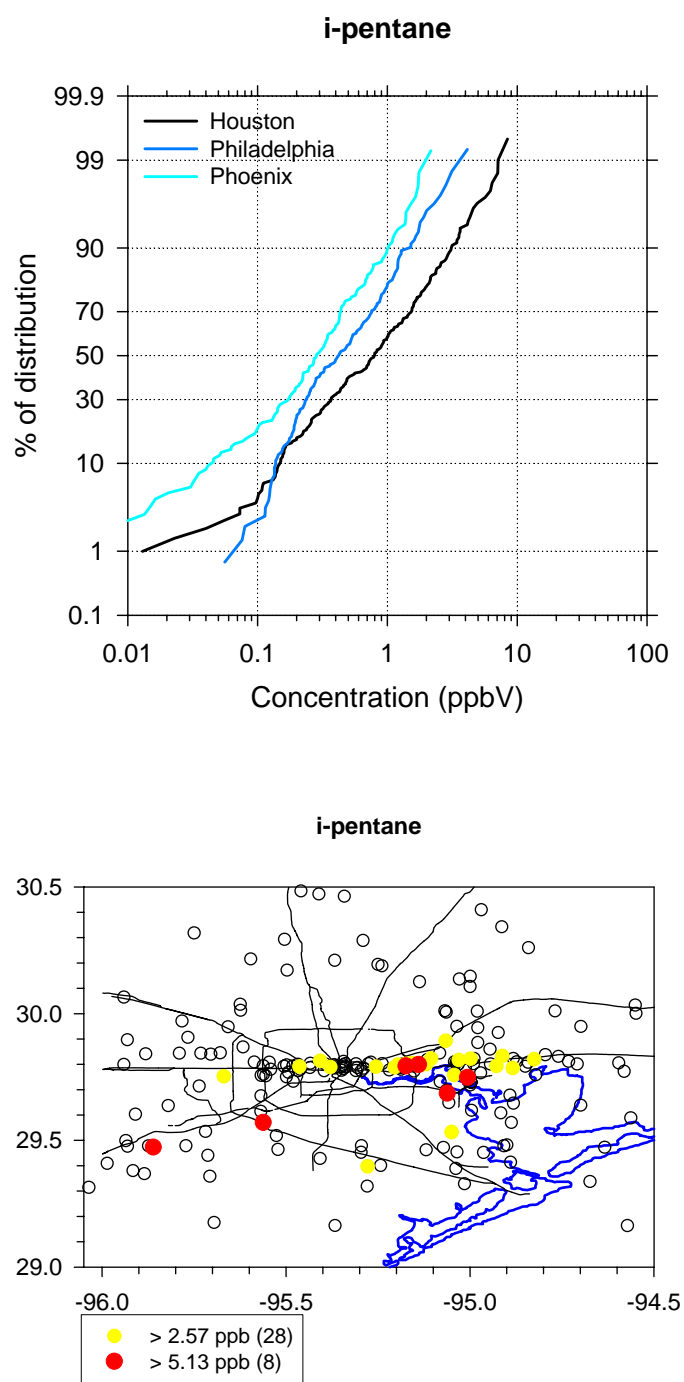


Figure 18 Frequency distribution and map for i-pentane. Same format as Figure 12.

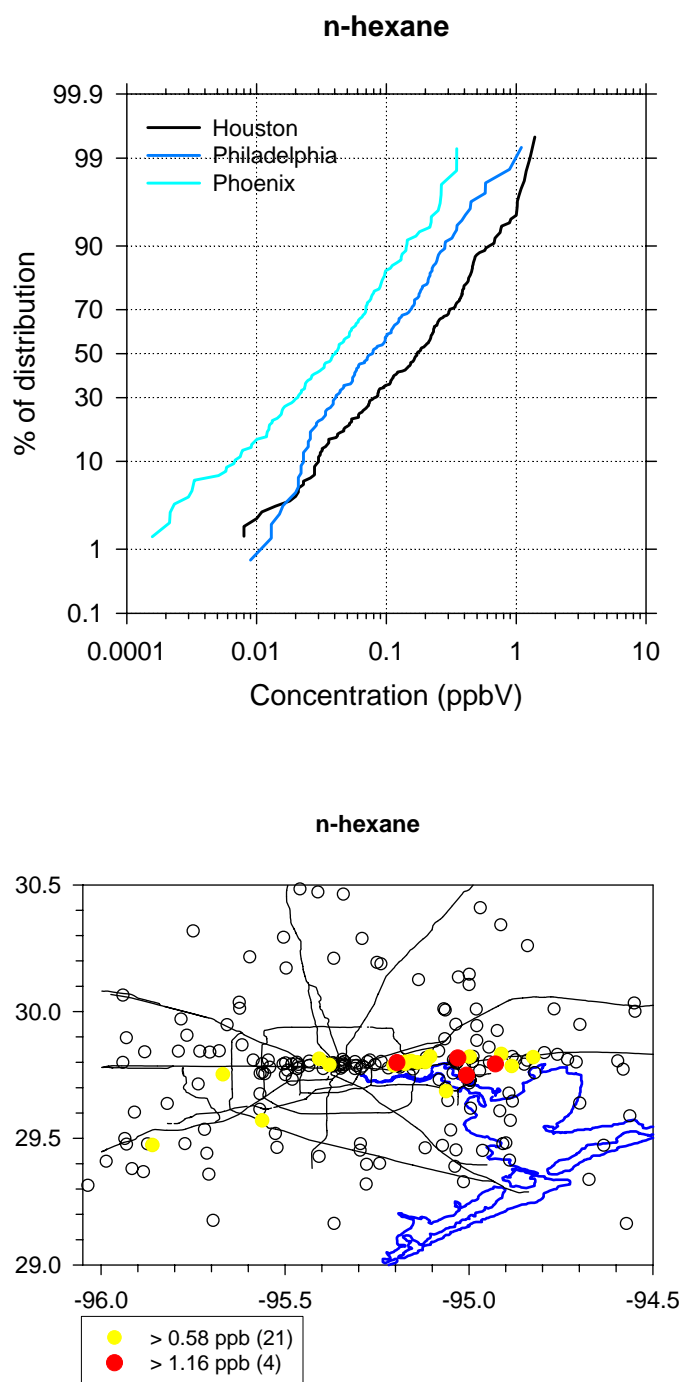


Figure 19 Frequency distribution and map for n-hexane. Same format as Figure 12.

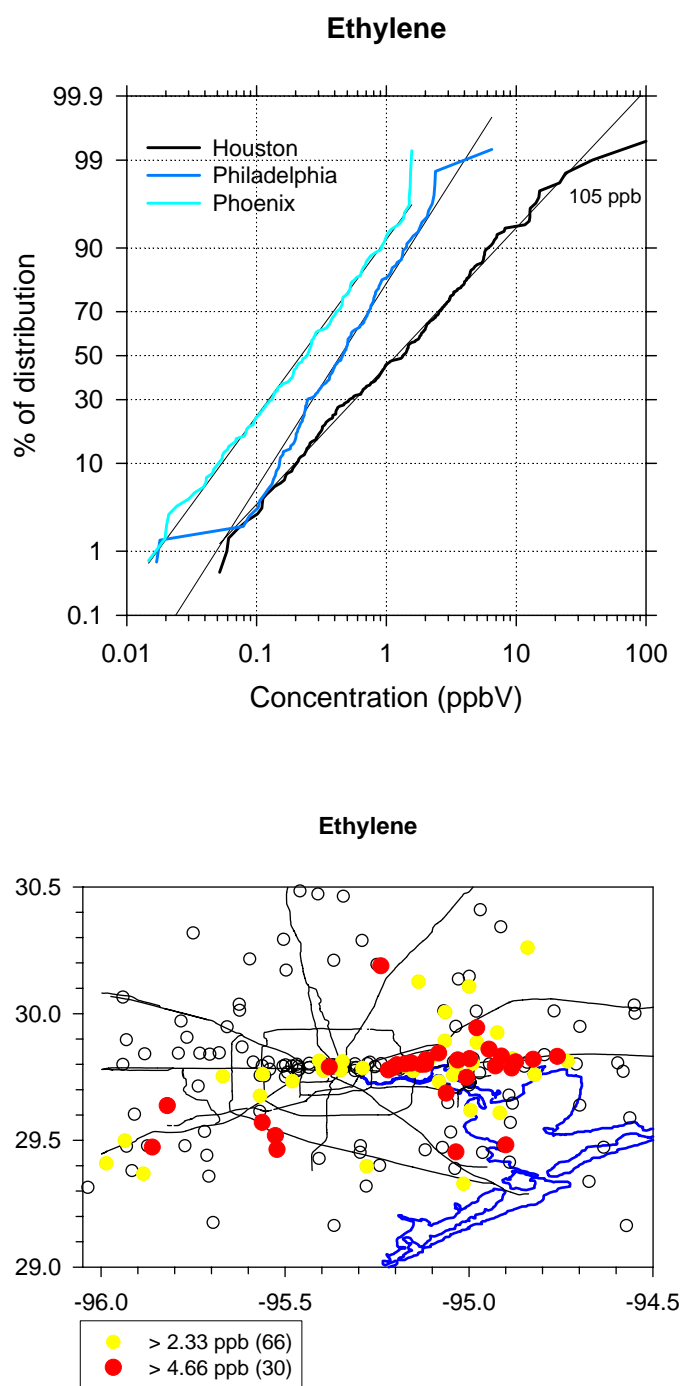


Figure 20 Frequency distribution and map for ethylene. Same format as Figure 12 except that linear least squares regression fit given by straight lines on top panel.

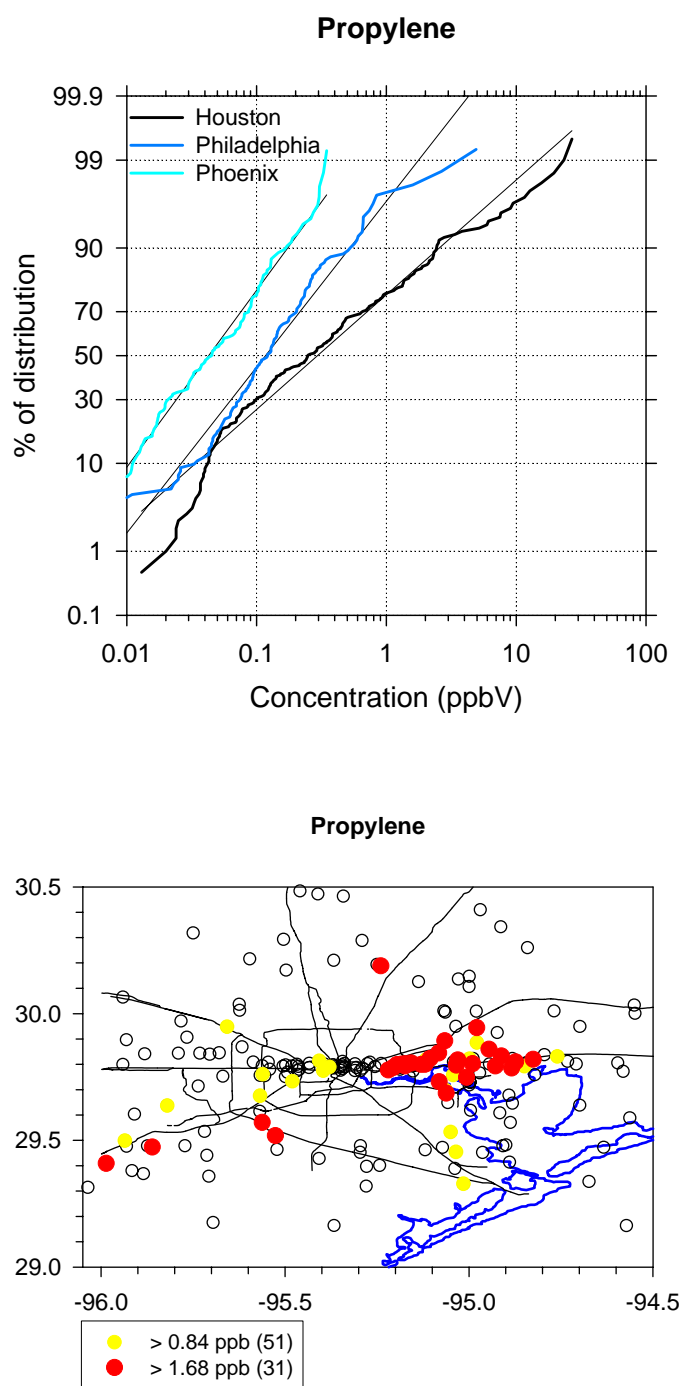


Figure 21 Frequency distribution and map for propylene. Same format as Figure 12 except that linear least squares regression fit given by straight lines on top panel.

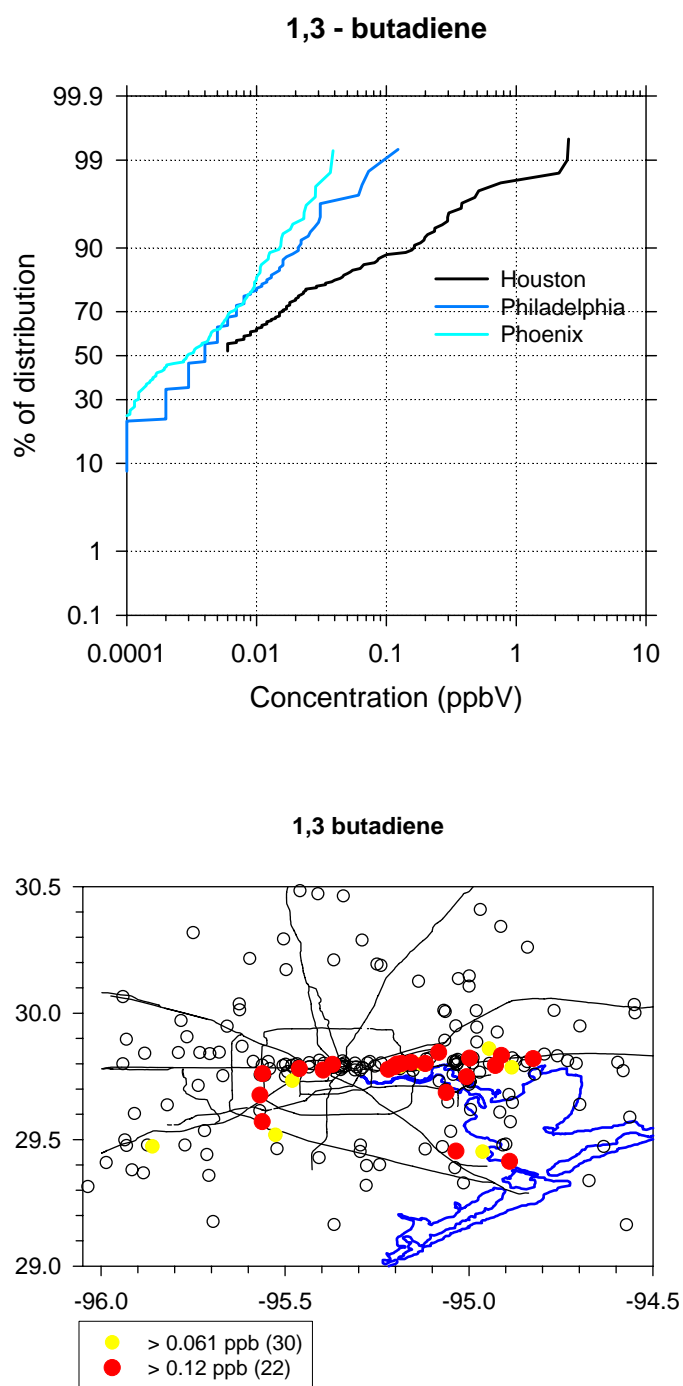


Figure 22 Frequency distribution and map for 1,3 butadiene. Same format as Figure 12. Note the high detection limit for 1,3 butadiene leading to a zero median when samples with concentrations below detection limits are counted as zeroes.

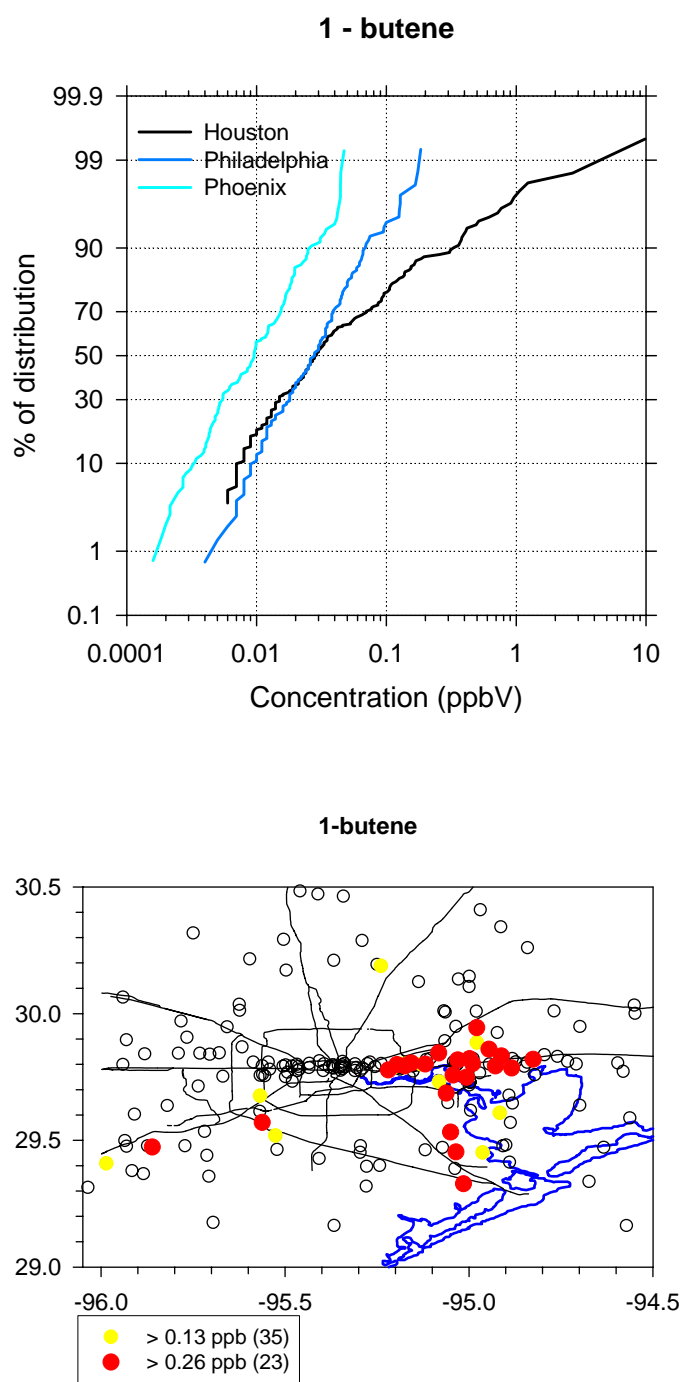


Figure 23 Frequency distribution and map for 1-butene. Same format as Figure 12.

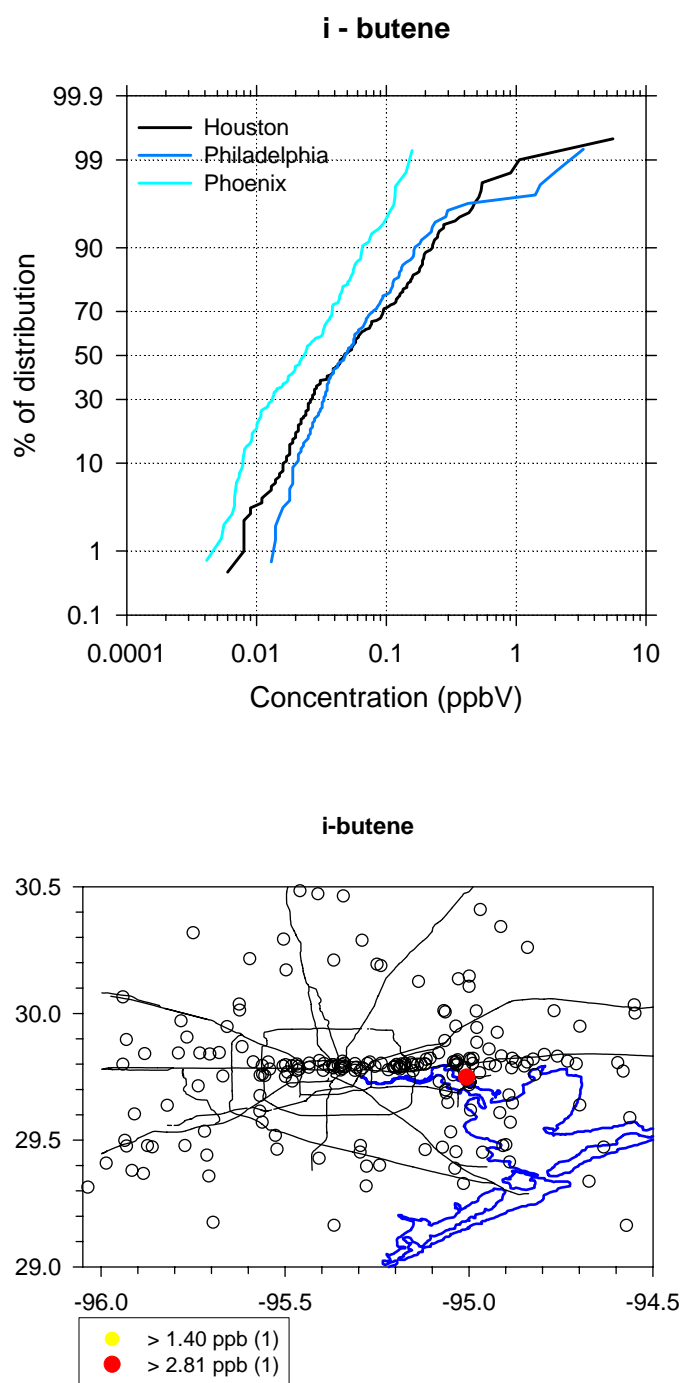


Figure 24 Frequency distribution and map for i-butene. Same format as Figure 12.

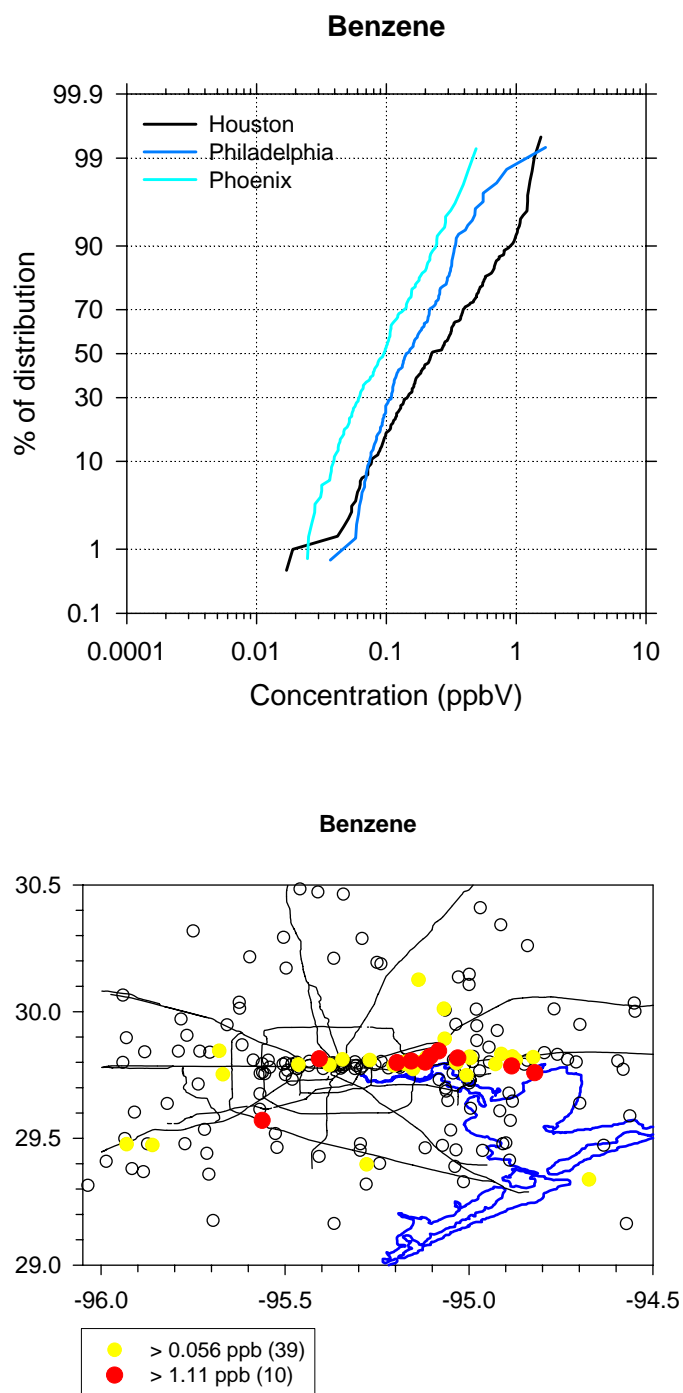


Figure 25 Frequency distribution and map for benzene. Same format as Figure 12.

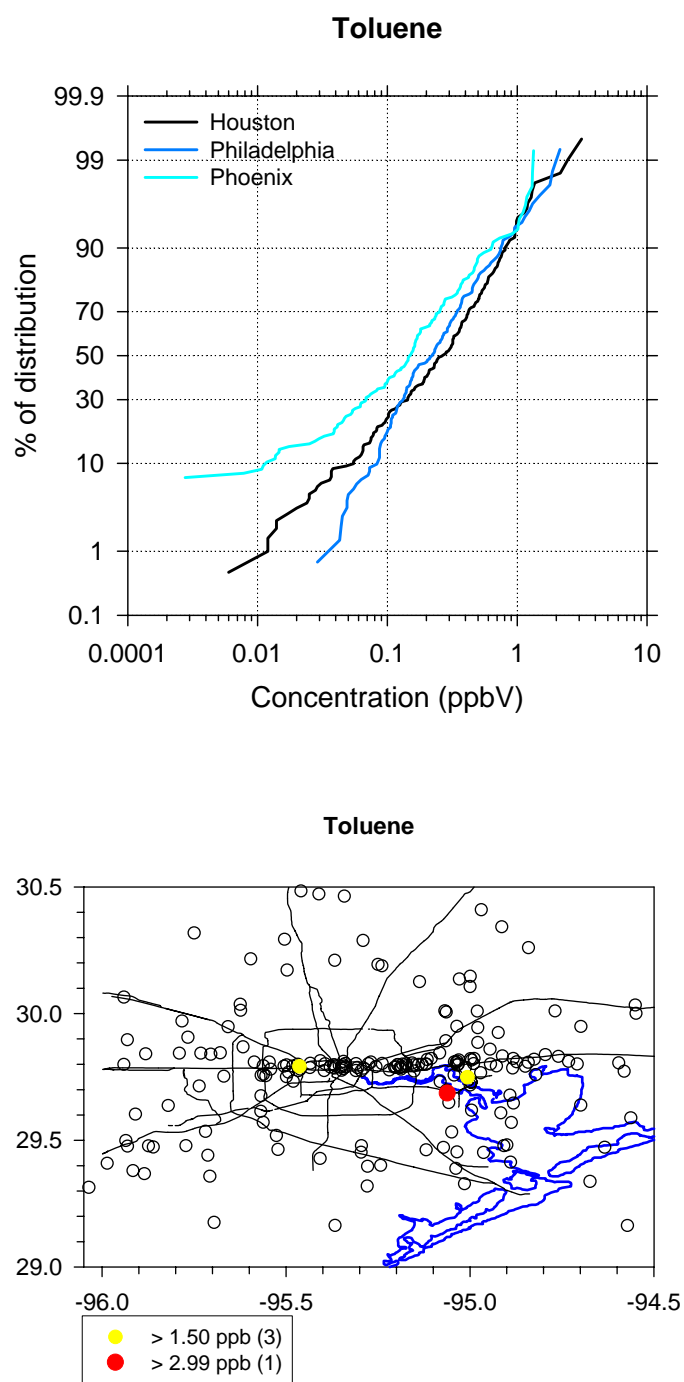


Figure 26 Frequency distribution and map for toluene. Same format as Figure 12.

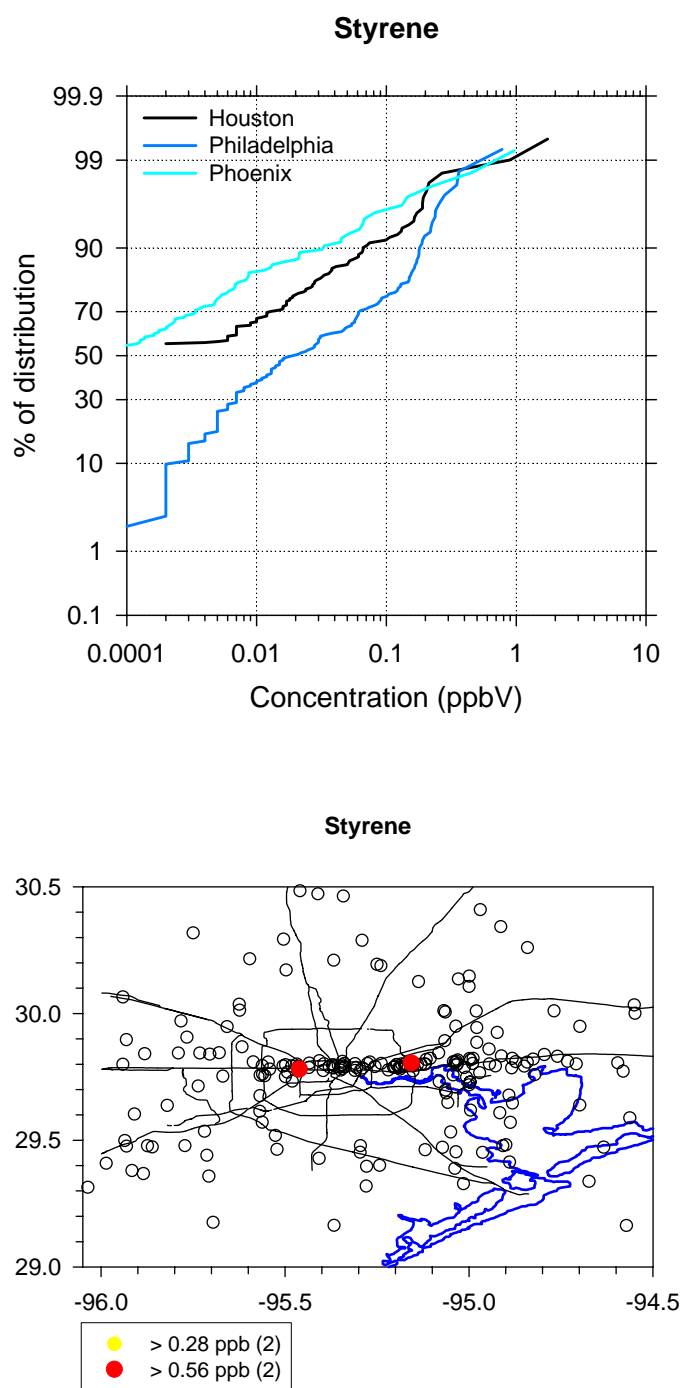


Figure 27 Frequency distribution and map for styrene. Same format as Figure 12.

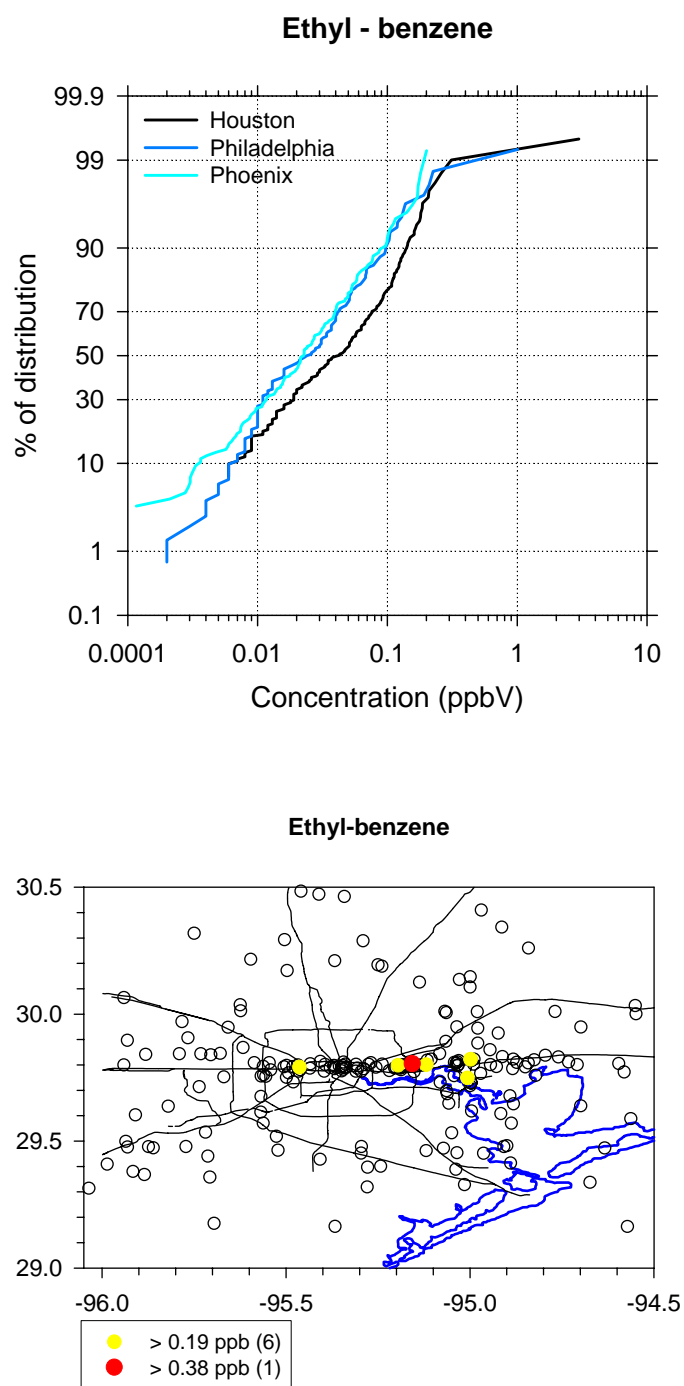


Figure 28 Frequency distribution and map for ethyl-benzene. Same format as Figure 12.

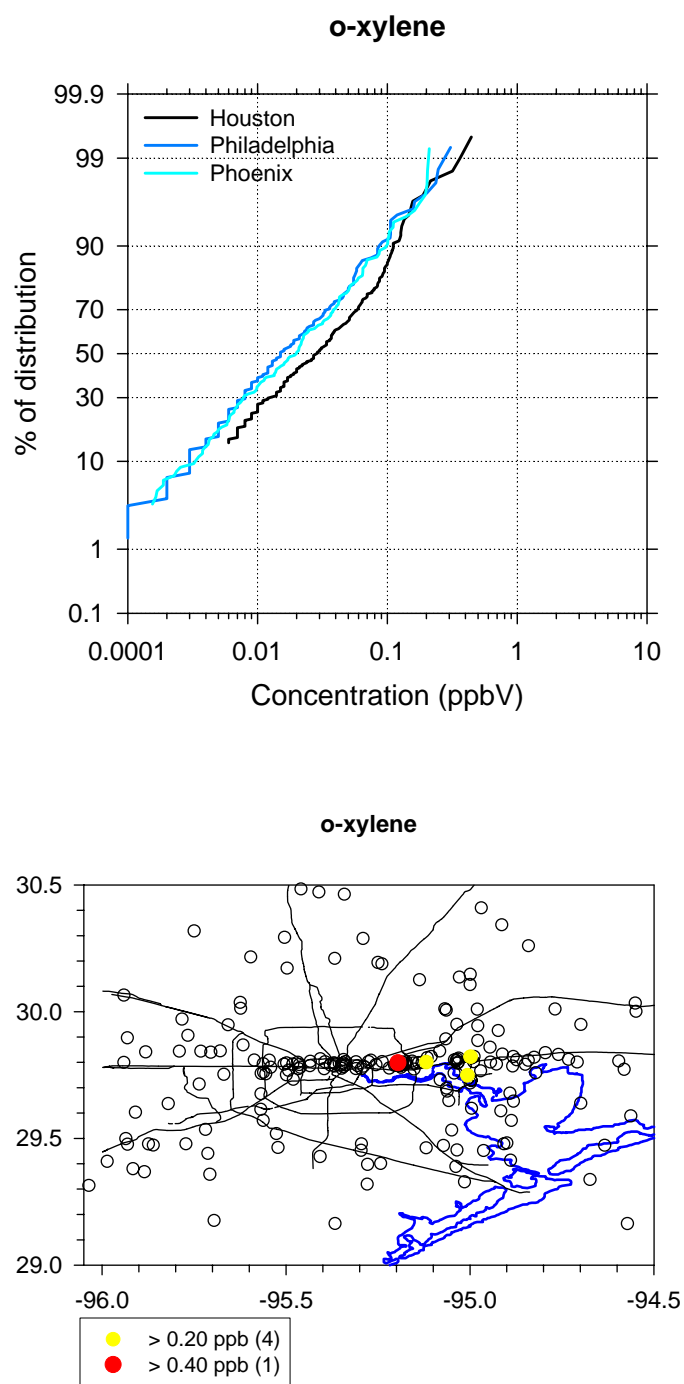


Figure 29 Frequency distribution and map for o-xylene. Same format as Figure 12.

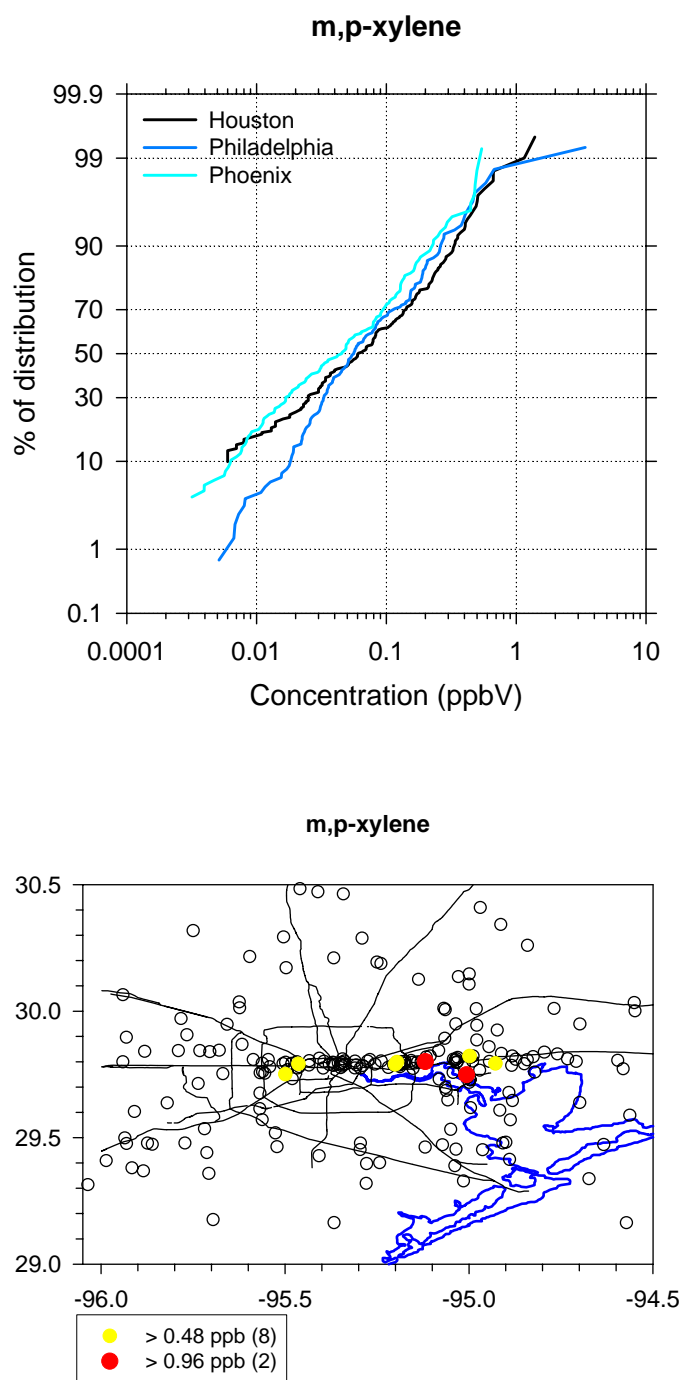
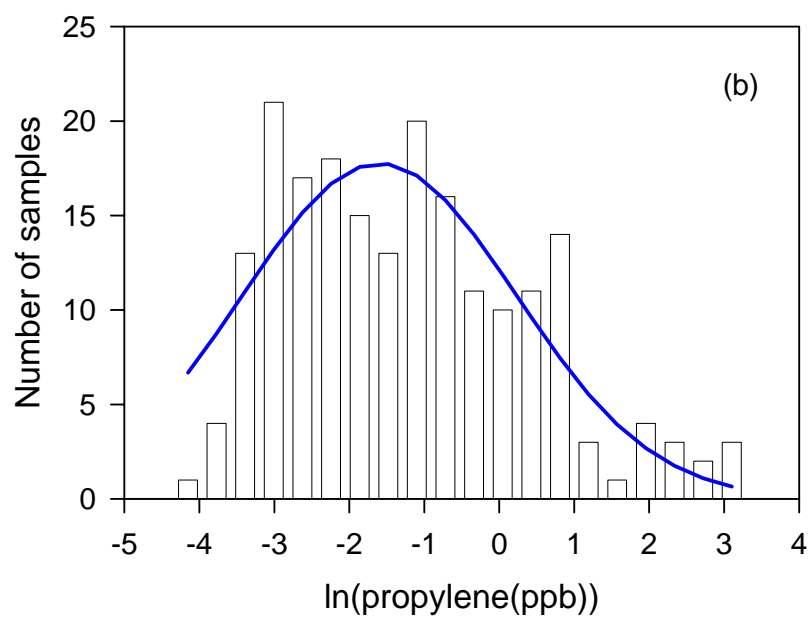
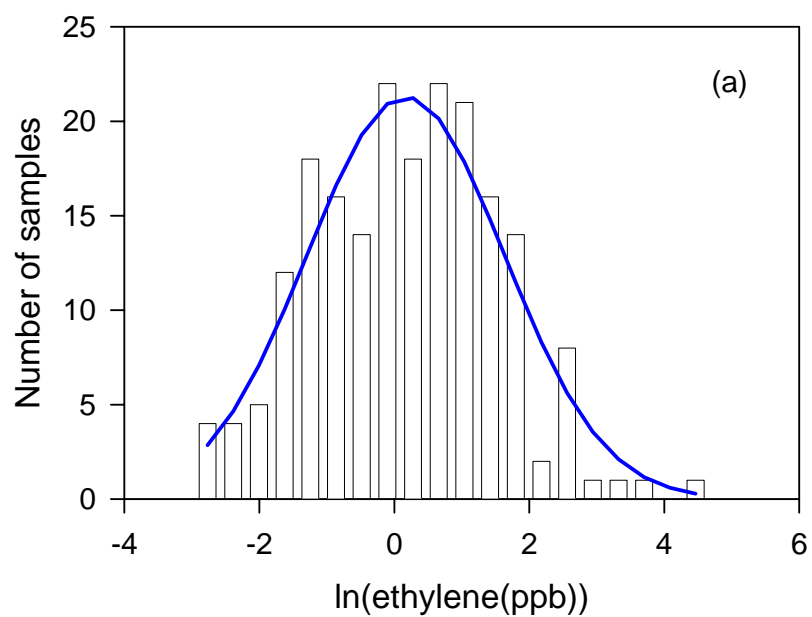


Figure 30 Frequency distribution and map for m,p-xylene. Same format as Figure 12.



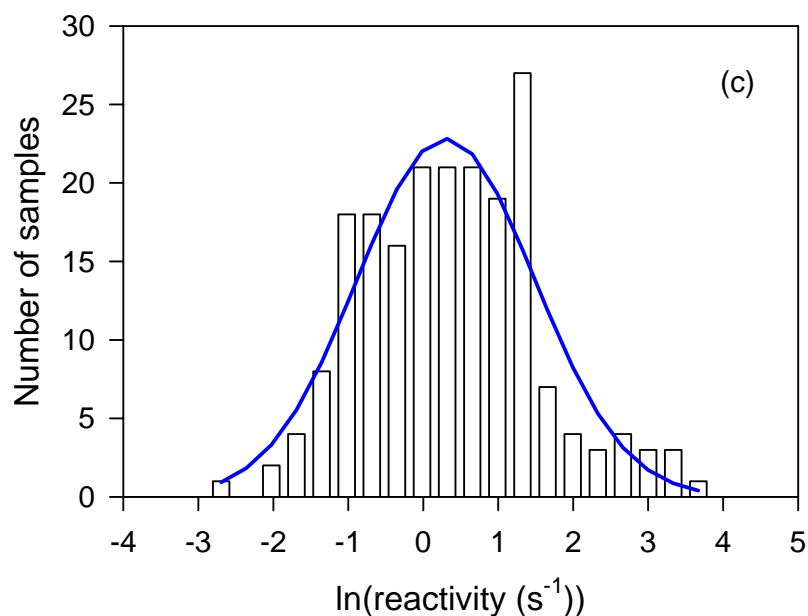


Figure 31 Histograms showing the number of G-1 samples in specified bins for concentration or reactivity. Twenty bins are equally spaced on a natural log scale. Curves are a Gaussian fit to the histograms. Because of the \ln transform, a perfect fit signifies that the functional form of the data is log normal: (a) ethylene concentration, (b) propylene concentration, and (c) total anthropogenic hydrocarbon reactivity.

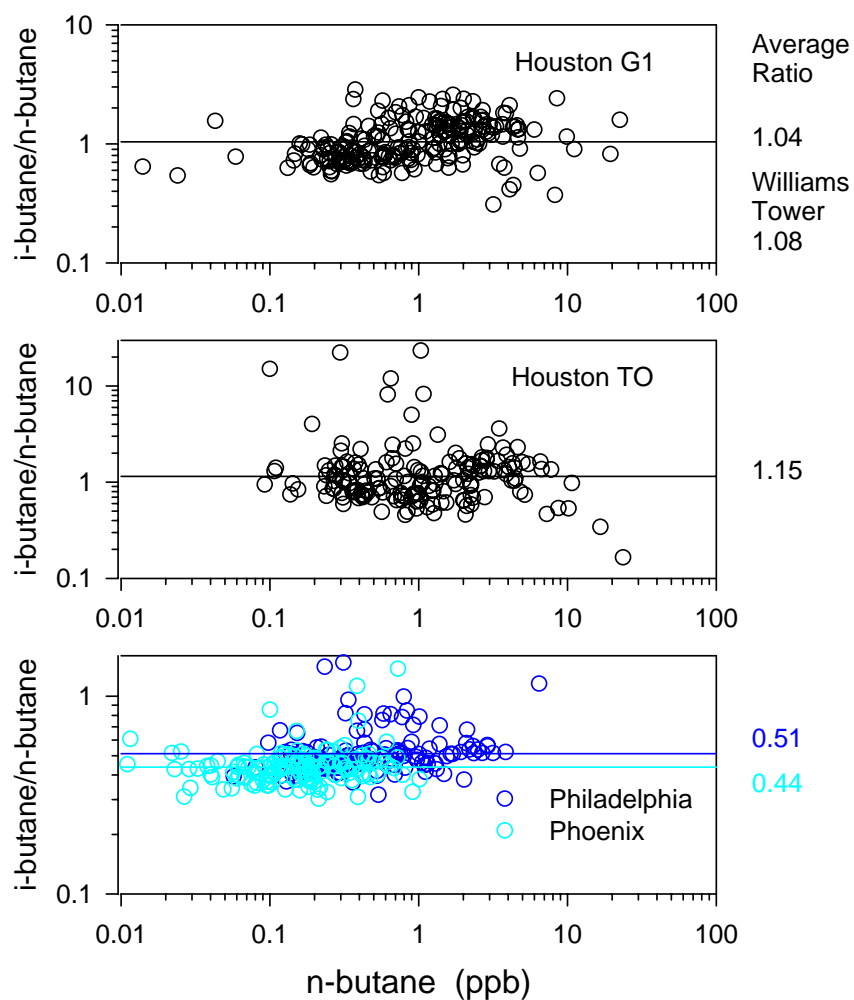


Figure 32 Log of i-butane/n-butane as a function of log (n-butane) for 3 data sets from Houston and for the G-1 aircraft observations in Phoenix and Philadelphia.

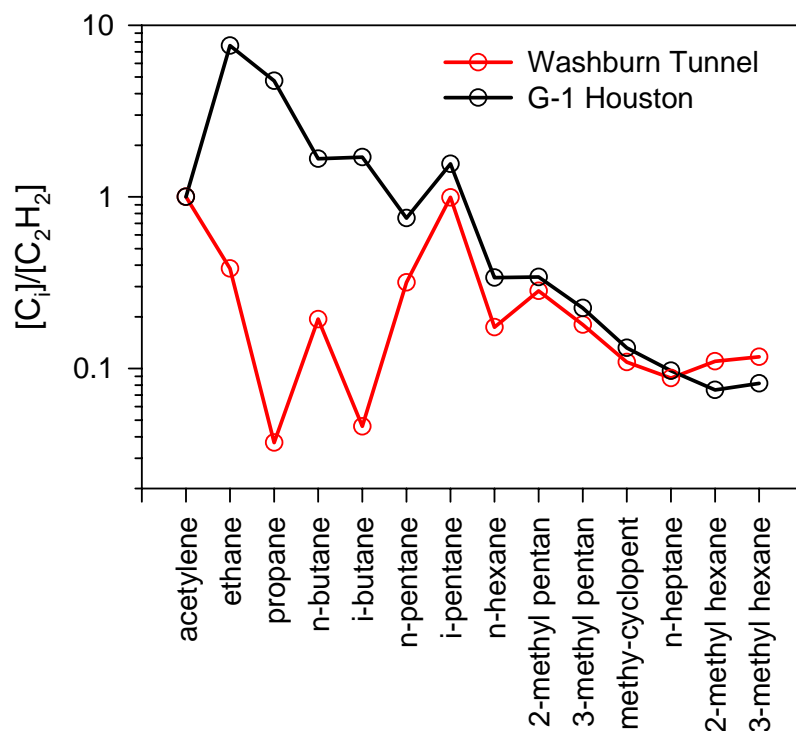


Figure 33 Comparison between normalized light alkane concentrations measured in the Washburn Tunnel and by the G-1. The Washburn Tunnel data has been normalized to C_2H_2 by taking the slope of a linear least squares regression of alkane vs. C_2H_2 . All species are well correlated with C_2H_2 ($r^2 > 0.9$) except propane and i-butane. Normalization for the G-1 data set is accomplished by taking the ratio of median alkane to median C_2H_2 .